UNIVERSAL
LIBRARY
OU_160435
UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 540.9/A73C Accession No. 9923

Author Armstrong. E.F.

Title Chemistry in the 20th Century. 192

This book should be returned on or before the date last marked below.

CHEMISTRY IN THE TWENTIETH CENTURY

CHEMISTRY IN THE TWENTIETH CENTURY

AN ACCOUNT OF THE ACHIEVEMENT AND THE PRESENT STATE OF KNOWLEDGE IN CHEMICAL SCIENCE

Prepared under the Guidance of a Committee representing the Scientific Societies with
DR. E. F. ARMSTRONG, F.R.S.,
as Chairman and Editor



LONDON: ERNEST BENN LIMITED
8 BOUVERIE STREET, E.C.4
1925

First Impression . . *April* 1924
Second Impression . . *June* 1924
Third Impression . *January* 1925

Richard Clay & Sons, Ltd., Printers, Bungay, Suffolk

PREFACE

THE aim of this volume is to present to the reader, by means of a series of monographs, a statement of the present position of Chemical Science in Great Britain, as illustrated by the exhibits in the Chemical Hall at the British Empire Exhibition (1924). It has been prepared under the guidance of a Committee representing the Scientific Societies with Dr. E. F. Armstrong, F.R.S., as Chairman and Editor.

The Committee has been fortunate in securing the ready co-operation of a number of distinguished men of science, who have contributed articles on their own special subjects: to them the Committee tenders its most hearty thanks.

In presenting this statement the Committee has had in mind the enormous expansion of the Science during the past decade, and the consequent specialisation which has taken place in its various branches. To such an extent has this developed, that the technicalities of one branch are sometimes unknown to workers in other branches. This volume, however, is designed for reading by all those, the world over, who have received, or are receiving, a training in science; and to this end the writers of the monographs have made their contributions in a form which it is thought will be acceptable to a very wide circle of readers.

The story told in these pages is a record of achievement which in friendly rivalry challenges comparison with similar work done in other parts of the world, and in Great Britain in decades gone by. It is offered as a contribution made by British men of science to the work of building up the Empire, which is commemorated more fully in the whole Exhibition itself.

W. J. U. W.

April 1924.

CONTENTS

PAGE

INTRODUCTION 11
By E. Frankland Armstrong, D.Sc., Ph.D., F.R.S.

THE *RÔLE* OF CHEMISTRY IN PHYSICAL SCIENCE 23
By Professor James Irvine Orme Masson, M.B.E., D.Sc.

THE STRUCTURE OF THE ATOM 43
By Edward Neville da Costa Andrade, D.Sc., Ph.D.

CRYSTALLOGRAPHY 56
(*a*) By Sir Henry Alexander Miers, M.A., D.Sc., F.R.S.
(*b*) By Thomas Vipond Barker, M.A.

X-RAY ANALYSIS OF CRYSTALS 78
By Professor Sir William Henry Bragg, K.B.E., M.A., D.Sc., F.R.S.

THE RARE GASES OF THE ATMOSPHERE 82
By Morris William Travers, D.Sc., F.R.S.

THE CHEMISTRY OF CARBON COMPOUNDS 88
By Professor Jocelyn Field Thorpe, C.B.E., D.Sc., Ph.D., F.R.S.

MILESTONES IN ORGANIC CHEMISTRY 122
By Professor Henry E. Armstrong, Ph.D., LL.D., D.Sc., F.R.S.

THE CHEMISTRY OF COLLOIDS 127
By William Clayton, D.Sc.

CATALYSIS 136
By Thomas Percy Hilditch, D.Sc.

THE FATS AND OILS 144
By John Allan.

THE SUGARS AND CARBOHYDRATES 151
By Principal James Colquhoun Irvine, C.B.E., LL.D., Ph.D., F.R.S.

CELLULOSE 159
By Charles Frederick Cross, B.Sc., F.R.S.

COLOUR IN NATURE 167
By Reginald Furness, M.Sc.

COAL-TAR COLOURS 179
By Ernest Arthur Bearder, M.Sc.

SYNTHESES IN THE TERPENE SERIES 187
By Professor George Gerald Henderson, M.A., LL.D., D.Sc., F.R.S. and Alexander Robertson, M.A., B.Sc.

THE ALKALOIDS 196
By Professor Frank Lee Pyman, D.Sc., Ph.D., F.R.S., and Thomas Anderson Henry, D.Sc.

THE NITROGENOUS CONSTITUENTS OF THE LIVING CELL 203
By Robert Henry Aders Plimmer, D.Sc.

PAGE

BIOCHEMISTRY AND FERMENTATION 216
By Professor Arthur Harden, D.Sc., Ph.D., F.R.S.

CHEMISTRY IN AGRICULTURE 224
(a) By Sir John Russell, D.Sc., F.R.S.
(b) By Harold James Page, M.B.E., M.Sc.

ALLOYS 243
By Professor Cecil Henry Desch, D.Sc., Ph.D., F.R.S.

POTTERY AND REFRACTORIES 249
By Joseph Burton.

FLAME, FUEL AND EXPLOSION 256
By Hubert Frank Coward, D.Sc.

EXPLOSIVES 265
By Sir Robert Robertson, K.B.E., M.A., D.Sc., F.R.S.

THE CHEMISTRY OF PHOTOGRAPHY 274
(a) By Sir William Jackson Pope, K.B.E., M.A., D.Sc., LL.D., F.R.S.
(b) By Walter Clark, M.Sc.

The Editors are indebted to the following for the loan of blocks and electrotypes :

To Messrs. G. Bell & Sons, Ltd., for three illustrations in Dr. Andrade's monograph, "The Structure of the Atom." To the Institute of Chemistry for Fig. 1 ; *to the Cambridge University Press for Fig.* 2; *and to Messrs. Longmans, Green and Co. for Fig.* 3, *of Mr. H. J. Page's monograph on "Chemistry in Agriculture."*

CHEMISTRY IN THE TWENTIETH CENTURY

CHEMISTRY IN THE TWENTIETH CENTURY

INTRODUCTION

By E. FRANKLAND ARMSTRONG, F.R.S.

"When I wander here, and there,
I then do most go right."

If a dispassionate comparison be made between civilisation as it is and as it was in the days of the Roman Empire, or in still more ancient Egypt, it will be found that whilst there has been but little progress in art or in literature or in politics either civic or national, there is a complete change in the life of the world as the result of the development of scientific method and its practical applications. To the average citizen this is distinguished from former ages above all by the development of machinery, yet it must be remembered that the progress in mechanical science has been the consequence of progress in the fundamental sciences of chemistry and physics. Because of their profundity, these cannot well be understood by the man in the street; indeed the hope of popularising the more abstruse facts of science is bound to remain an ideal.

The object of this volume is to put on record our knowledge of chemical and physical science in Britain and the Empire with particular reference to the progress during the last thirty years, a period which has been exceptionally prolific in new ideas.

The first few articles indicate in simple language the development of modern theories and give a clear picture of to-day's position and of the directions in which further progress is to be anticipated. The more specialised chapters describe the actual progress more especially of British investigators in certain selected fields which particularly lend themselves to such treatment. Other sections again deal with the more practical aspects of the subject, and illustrate almost with kaleidoscopic rapidity the progress in certain selected industries consequent on the application of the new theories.

British chemists have always been willing to give full recognition to the work of their distinguished foreign colleagues, and this is the wish of each contributor to the volume. As, however, the main object has been to emphasise the work of British enquirers, it is possible, indeed unavoidable, that much foreign work has been passed over without mention.

In a recent pamphlet Mr. John Galsworthy has suggested that the world is more ready to use science and invention for destructive purposes than for social progress and that it is "more hopeful of perfecting poison gas than of abating coal smoke." It is an object of the following essay to show that this view is surely based on a misconception, due to the fact that we view the happenings of the world to-day in a mirror prepared by a Press which only reflects the sensational. Scientific work leading to social progress is going on apace; still it is only when it approaches the sensational that it becomes good copy. The chief object of our great explosives industry, for example, is to produce explosives for coal and other forms of mining, research is constantly being carried on to make these both safe and certain and to control their action: the experience so gained is necessarily available when explosives are required for war purposes. During the Great War, when destruction was the sole object of humanity, all the agents used were created solely as the result of the experience gained in times of constructive effort, the only new factor being the provision of money and the facilities which money brings for research

on a scale never before even imagined. Naturally the rate of invention was increased, but the production was in no way commensurate with the cost. If the world could afford to subsidise research on the same scale, during a decade under peace conditions, our rate of progress would be beyond all belief, though it must be confessed that great social disturbances might follow, as probably the world would be unprepared to receive the new wonders.

The cultivation by the nation of a scientific as opposed to a literary–classical habit of thought is largely a matter of education; the change cannot much longer be delayed if we are to retain our place among the nations. Scientific enquiry is coming to be recognised more and more as the basis upon which advance in industry rests. Whatever may be the views on this controversial subject, few will deny the need for a proper appreciation of scientific method by the multitude; many are at last beginning to realise the part that science has played in making the real history of the world.

It is obvious that the progress of chemical science depends on the continuous prosecution of original enquiry. We look with confidence to the University Laboratories for this, though their work will be supplemented to some extent by private effort and by the work of Research Associations, which latter, however, is mainly directed to special ends. An honourable obligation is cast upon us individually and collectively to see that the endowment of research chairs, the equipment and maintenance of laboratories, and the supply of competent assistants are adequate.

Above all, it is essential that the research laboratories be placed under conditions of absolute freedom, as such work—the pursuit of truth for its own sake—cannot be forced; the wind of genius bloweth where it listeth. It has been truly said recently that in the pursuit of science the chief requirement is character; to use Sir William Bragg's words, " research is not a religion, but the act of one."

The word research is so often used, not to say abused, nowadays that we are in danger of regarding as scientific enquiry much which is in reality mere exercise or even advertisement. It must essentially be carried out with the object of understanding the purpose of the Universe. Each school should have its broad plan of campaign, so that the section of the field explored by any particular worker should fit in with and have a bearing on the work of all the other enquirers in the laboratory. It was only by such systematic investigation that the great achievements of the past were made possible, and the modern tendency towards advertisement exemplified in the publication of immature work is to be deprecated.

Chemistry, in particular organic chemistry, is perhaps to-day at the parting of the ways, and we may well be on the eve of another great advance due to the birth of new views of structure. Earnest workers in all branches of the science are making strenuous efforts to see behind the curtain and are converging to a common view—a sure sign that a renaissance is at hand.

The question of structure is the basis of all the articles in this volume; it is therefore desirable to dwell a little fully on the subject in order to make clear the position which the chemist has to-day reached. Everything tends to show that function and structure are most closely connected—odour, taste, colour, physiological effect are specific rather than general properties, each conditioned in its particular variety by some special structure. The most suitable unit for consideration is the molecule; this is to the chemist what the pound sterling is to finance; with it in mind, he describes reactions and builds formulæ, he weighs and measures it: in short, it is a real and definite presentment. Molecules can be of all sizes and of every degree of com-

plexity, though actually so small that no microscope will show them. The nature of gross matter is determined by the properties of the individual molecule.

The molecule is built up from the atom, the atom of each element having specific properties according to an orderly scheme of nature which enables the chemist largely to predict their behaviour. The atom of the beginning of the century was the *hypothetical* smallest subdivision of matter; the atom of to-day is a *real* object of definite size and shape. The characteristic property of the atom is that of valency, which is the measure of its capacity to unite with other atoms to form the molecule. This property was at first regarded as merely arithmetical, but the genius of van't Hoff and of Le Bel conceived it as a geometrical attribute and gave to the atom a definite shape in space. This discovery, in particular that of the tetrahedral nature of the carbon atom, following the conception by Pasteur of the geometrical asymmetry of the carbon atom, gave a new impetus to the chemistry of carbon compounds which we term organic chemistry. Professor Thorpe's article describes in a most lucid and fascinating manner how, as the result of what may be termed the synthetic or "compound-making" phase, organic chemistry has become almost the most exact of the sciences, so that our knowledge in detail of the exact molecular structure of carbon compounds is little short of remarkable.

Our present conception is that the carbon atom has tetrahedral properties in the sense that it has four affinities which operate practically in the direction of the four radii proceeding from the centre towards the four solid angles of a regular tetrahedron. Nothing is more surprising than the completeness with which the vast array of facts included in organic chemistry may be ordered by reference to the tetrahedral model.

The development of organic chemistry is nothing short of marvellous. In 1885 it was possible to write that the physiologist complained that probably 95 per cent. of the solid matters of living structure were pure unknowns and that the fundamental chemical changes which occur during life were entirely enshrouded in mystery. To-day, fats, sugars, proteins, tannins, alkaloids, terpenes, colouring matters, purins have all been conquered by the chemist, and even starch and cellulose have begun to yield up their secrets; the nature of only a few per cent. of the components of organic structure remains unsettled, and we are far forward in our understanding of vital problems. No one has contributed to this success in greater measure than Emil Fischer.

Attempts to resolve the molecule into something smaller, as, for example, by electrical energy, result in the formation of "radicals," charged respectively with positive and negative electricity, which migrate to the respective poles of the circuit—these electrically charged parts are called ions. Dr. Masson's article sets out in the clearest manner the modern conception of the ion and how, for example, our views have progressed so far that a piece of copper is not regarded merely as a mass of atoms, but as an assemblage of positively electrified atoms or ions with which are interwoven the compensating negative units, the electrons.

Discovery with regard to the molecule and atom has passed through several stages. First came that of "Dancing molecules," *i.e.* the explanation afforded by the kinetic theory that gaseous effects are consequences of the motion of the molecules. Then, much later, the discovery by J. J. Thomson that electricity is a material, that its "atoms" are the electrons which in turn constitute the atoms of matter. The weighing of the atom in terms of the charge it carries in electrolysis, a conception we owe to Faraday, has been finally effected by the measurement with extraordinary precision of the absolute value of the unit charge—the electron—by Millikan. The counting of individual atoms, begun with Crookes' spinthariscope and culminating

in the work of Rutherford on the α-particle (Helium) discharged in radioactive change, has led directly to the determination of the composition of the atom and finally to the conception that every atom contains electrons together with a positively charged nucleus, very small compared to the whole atom, but so dense that it contributes nearly the whole weight of the atom. One atom differs, it is thought, from another in the magnitude of the positive charge of the nucleus, which determines how many electrons it can hold and hence all its physical and chemical properties.

One of the problems of the moment, at last year's meeting of the British Association, was, as humorously put by Sir Oliver Lodge, why when one end of a stick is raised from a table the rest of it also comes up: in more precise language, the question of the nature of cohesion and intermolecular forces. To solve this problem chemists are at work on the atom, on crystals, and on alloys, to say nothing of the recognition, in still other fields, of monomolecular films.

The method of X-ray analysis, developed in this country by Sir William Bragg and his son, is opening up a new method of attack on many of our problems. In the past, the properties of gases were studied when it was required to gain information about molecules; to-day it is possible to study matter in the crystalline form. The old view, in which atoms and molecules were pictured as centres of forces exerted in all directions, was satisfactory for gases and liquids, but failed when applied to the solid.

The chemist has to deal with matter in the crystalline state. Seeing that this is the state naturally assumed by a substance when it becomes solid, it must be the expression of the manner in which molecules or particles of the crystallising substance are arranged in space. If we can gain an idea of the structure within the crystal, then our knowledge of the constitution of matter is remarkably near to being complete. So rapid has been the progress in this direction during the last few years, that no apology need be made for the somewhat unusual amount of emphasis of crystallography, including X-ray analysis, in this volume. It is appropriate that the subject should be introduced by Sir Henry Miers, who has done so much to advance the teaching of crystallography in this country. The very thorough and broad treatment of the subject in Mr. Barker's essay is completed by Sir William Bragg's lucid account of what X-ray analysis has accomplished. Very briefly, our ideas of the crystal have reached the stage that it consists of units of pattern, larger than the simple molecule, as they may consist of several molecules. In the case of salt, it is considered that four molecules represent the minimum amount of matter involved in the creation of a crystal unit or cell, a quantity which, as Barker shows, is too small to be apprehensible by any known method of investigation. These units lie on the lines and planes of a lattice, the whole structure being an orderly arrangement. The X-ray method has allowed of the measurement of the distance between the sheets. The forces which hold the molecules together involve the sh[illegible]g of the electrons. In the case of carbon, it would appear that each atom has four others ar[illegible]ged about it in tetrahedral fashion, each sharing, it is suggested, two electrons with each of its neighbours, so that the normal stable shell of eight electrons is completed. The crystal structure is very empty, being but a lattice in space. As Sir William Bragg describes the crystal of the diamond, two types of arrangement are perceptible, namely, the hexagonal ring and a long continuous chain of carbon atoms. The agreement between the real molecular architecture of the crystal and that which the chemist has been engaged in elaborating, inspired by the genius of van't Hoff, is remarkable.

According to modern views, the powerful forces between atom and atom, molecule and molecule, are limited in their effective range of action to distances smaller than that between

the units in the crystal, consequently in such compounds as the fatty acids there is no influence of the ends upon the atoms in the middle. In passing from one acid to a homologue of greater molecular weight each addition to the thickness of the ultimate flake is made in complete independence of the previous length, as if the only thing that mattered were the attachment of one carbon atom to the next. It is of interest, in view of later arguments in this article, that the ultimate flakes of the crystals of fatty acids are regarded as the monomolecular films studied by Langmuir.

Valency to-day is anything but a simple conception, but its proper understanding is one of the most pressing of the issues of to-morrow, as the problems of structure are at bottom all valency questions and the nature of valency eludes us; therefore a few introductory words seem desirable.

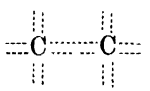
In order to explain the combination of the elements with one another, each atom of every element is supposed to have a certain definite number of centres of attraction or bonds, as they were first called by Frankland, by which alone it unites with other elements. In the case of carbon compounds, which are distinguished from those of all other elements by the ease with which carbon combines with itself, it is found that two carbon atoms may be united by two or even three out of the four bonds producing unsaturated compounds, as, for example, ethylene and acetylene.

$$>C=C< \text{ and } -C\equiv C-$$

This conception has been fully justified by the developments which followed from its introduction into organic chemical theory; it is true to say that the more important organic compounds belong to the unsaturated type, because it is this class of substance which is most active and capable of transformation.

But why should the "union" of two carbon atoms by a "double" or "treble" bond lead to greater susceptibility to chemical change? The answer to this query depends on the precise meaning to be assigned to the terms "union," "bond," or "linkage," in this connection. If, as was probably at first the case, the natural idea of tensile strength be connected with the phraseology used, it is obvious that the "union" may be likened to that effected by mooring two boats to each other with a wire hawser—if two hawsers were employed the vessels would be held together twice as strongly.

In fact, however, the attraction between atoms is fundamentally electrical and the actual "union" is a bundle or "Faraday tube" of electrical lines of force. It is obvious, therefore, that the attachment of two atoms together by means of two such pencils of electrical energy will be likely to lead to distortion of the respective force fields and consequently to a condition of less genuine molecular stability (which implies reactivity). The modern idea of union may be diagrammatically indicated in a crude way as



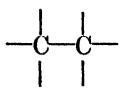
single linkage

and

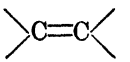


double linkage

rather than



and



This view has only been realised to the full during the present century, especially since the octet theory of electronic atomic structure was formulated; the necessity for premising that a double " bond " was a weaker " union " than a single " linkage " was grasped much earlier and found expression in the more or less tacit assumption—provoked by many experimental facts—that when atoms were " united " by means of more than one of their respective centres of attraction a certain amount of chemical affinity was left free or " unbound " at each atom, thus allowing for its abnormal activity.

This excess of chemical force came to be termed " residual affinity," or, more briefly, " unsaturation," and it was ultimately evident that in all elements or compounds, except the inert rare gases, there must be centres at which a certain amount of residual affinity (*i.e.* more or less free chemical energy) was available—otherwise chemical change could never take place.

More specific applications of these views to the behaviour of certain organic compounds have been made by Thiele (who assumed that the original bonds or valencies could be in a sense subdivided in certain cases, leading to what is known as the development of " partial valencies "), by Werner (who first introduced the conception of a general radiation of chemical affinity from an atom rather than separate rays of affinity corresponding in number to its numerical valency), and by Flürscheim, Robinson, and Lapworth (who have respectively applied the more recent conceptions of the electron theory to the case of organic compounds), but the subject then becomes somewhat too abstruse to be usefully dealt with in this book.

In practice, it is not the behaviour of single relatively small molecules which interests those immediately engaged in the arts and industries, but the properties of large aggregates of molecules which of late years have been conveniently designated colloids. In this field also, structure plays an all important part in influencing properties : its real significance has, indeed, yet to be grasped. As Mr. Clayton points out, every structure assumes special properties and a special behaviour when its particles are so small that they can no longer be recognised by the microscope though they are still far too large to be called molecules. The present idea with regard to liquids, and, indeed, to solids also, is that the molecules are orientated in layers in definite order, attractive forces also being at work between each layer and that next to it. The surface layer thus becomes the main factor determining surface tension and other surface properties, including chemical action, and there is much evidence that the molecules at the surface are so orientated that the more active portions are directed inwards and the less active outwards to the air. In the liquid paraffin hydrocarbons, for example, the terminal CH_3 groups are believed to form the surface layer, no matter how long the chain may be; this assumption is in agreement with the fact that they all have the same surface energy. When two liquids, for example oil and water, are in contact there is said to be an affinity between like parts or, in more exact language, the oxygen atoms, possessing high residual affinity, evidence a mutual attraction. Thus, when a drop of fatty acid is placed upon water the molecules become so orientated that the COOH group is attracted to the interface, the CH_3 end of the molecule turning towards the organic liquid, that is to say, to the air, when the layer of fatty substance is of molecular thickness.

The extension of this view to the occurrence of chemical action at the surface of solids—a phase of catalytic action—is fraught with the deepest consequence, as it affords some clue to the actions which take place at the active surfaces forming the cell-walls in the living organism. The proof of orientation of the molecules at a surface involves the adoption by the chemist of the idea of some sort of momentary combination or other loose form of association at the surface,

though some are content with the use of the phrase " adsorption," indicating mere local concentration. It requires, further, either the rearrangement of structure necessary to make tl e two surfaces fit, such as is only possible in a very limited number of cases, in which one of the substances concerned has a very simple and certainly not an asymmetric structure, for example, the hydrolysis of fatty esters by lipase. Alternatively, it necessitates a directly compatible structure, before there can be any association. This has been definitely proved to be the case in regard to interactions between the sugars and the plant and animal enzymes which hydrolyse them in so selective a manner. Only sugars of certain very definite molecular architecture are compatible with and hydrolysed by the enzyme. The slightest variation in structure means that there is no action. Two kinds of catalytically active colloid surface can in consequence be pictured. The one is exemplified by a metallic catalyst, in which a clean pure metal is the agent in so fine a state of division that the active surface exposed is of maximum extent. The other is a complex organic substance of high molecular weight containing several radicals; probably it possesses an elaborate structure, in consequence of its molecular complexity, so that certain groups are exposed and chemically active at the surface, which, to secure the maximum effect, must be as clean and as great as possible; whilst certain other groups are either masked by being directed away from the surface or internally neutralised or rendered inoperative in some other manner (steric hindrance).

If the enzyme be such an organic complex we could never expect to isolate it and characterise it in its unit state as some purists demand, though the possibility of effecting its synthesis is not excluded.

If space permitted, it would be tempting to pursue this section of our enquiry much further; enough has been said to show how the conception of an orientated active structure, at the surface of a colloid aggregate, might endow it with selective powers of so fine a nature as almost to merit the description of intelligence : the further prosecution of research on these lines may well serve to bridge the gap between us and the full understanding of vital activity.

It is next to impossible for the layman to form any proper appreciation of how far the results of chemical science are of influence in his daily life, still more to what an extent they are likely to come to his assistance in the future. He is more or less aware of the way in which the purity and quality of his food are watched over, both by the professional analyst and by the chemist at the food factory, though an ignorant Press is more prone to accuse the latter of the crime of substitution, not to use a harsher word; an accusation which is even further from the truth than most statements of this kind. To feed the teeming multitudes in our great cities, on ships and in the barren places of the earth, to say nothing of a modern army, would be impossible without the discoveries made by the chemist regarding sterilisation and the preservation of food in non-poisonous, cheap, metal containers. Even so minor a point as the most suitable kind of glass to be used as a container of food products is receiving the attention of a committee of glass technologists.

As will be shown under the heading of Agricultural Chemistry, the productivity of the soil and the quality of the crop have been greatly enhanced by the activities of the chemist, so that the daily loaf from the time of selecting and sowing the seed, manuring the land, harvesting the seed, and its passage through the rolls and bolting sieves of the miller to the doughing tub and oven of the baker, never escapes the vigilance of the chemist; some day he may even succeed in having it delivered to the consumer wrapped in clean paper.

Refrigeration is to-day in itself an applied science with the dignity of a special international congress, which will be in session during the period of the Exhibition. It is based very largely on the researches of a long line of distinguished chemists made with the object of producing the low temperatures required to liquefy, one after the other, the so-called permanent gases.

Thus chlorine was first liquefied by Northmore in 1806, and a few years later, exactly a century ago, Faraday liquefied a number of gases, including sulphur dioxide, carbon dioxide, and ammonia, by the combined influence of pressure and cold. His method was to seal up in a strong glass tube bent to the form of the letter U the materials to give the gas, then to generate this in one limb, whilst the other limb was cooled in a freezing mixture. It was Andrews who first showed the existence of a critical temperature for each gas below which alone it can be liquefied by pressure.

Before 1877, all the then known gases except hydrogen, oxygen, nitrogen, carbon monoxide, methane, and nitric oxide had been liquefied. On December 24th, 1877, Cailletet and Pictet announced the liquefaction of oxygen and carbon monoxide. Then the attack was begun again upon the other " permanent " gases at the Royal Institution, especially hydrogen. Liquid air was made a commercial possibility, and with its aid in 1895 Dewar was able to cool even hydrogen sufficiently to reduce it also to the liquid state. Liquid hydrogen in its turn, in the hands of Onnes aided by the Dewar vacuum vessel and the Dewar charcoal absorbent, was the means of effecting the liquefaction even of helium, the most permanent gas of all known, with which a temperature only 1° above that of absolute zero has been attained.

The story of the liquefaction of hydrogen and later of helium is one of the epics of chemical history—as is still more the whole chapter of the discovery of the rare gases, about which Dr. Travers writes so feelingly, and with the knowledge born of his own personal participation in the quest. Just think of the facts—scarce thirty years ago no scientific worker had even dreamt of the existence of the inert gases, and yet they were all around us, in the very air we breathe; moreover, a hundred years before Cavendish had indicated a clue to their discovery. In quick succession five new elements were discovered; one of them, helium, which has proved to be the most wonderful of all, had been already recognised as present in the sun by its characteristic spectrum and actually named by Frankland and Lockyer, its discoverers. To-day we, or at least our American cousins, fill an airship with this gas—Ramsay's discovery—without causing undue excitement in the world at large. Argon is now so common that it is used in filling the ordinary " gas-filled " electric lamp, neon replaces it in some illuminated signs. Never before have the results of abstract science so soon become of value in industry.

Few indeed will associate the now indispensable vacuum flask with low temperature research : this was Dewar's greatest gift to the nation and his name should always be associated with it. Both in its primary glass form and as the still more original metallic vessel with an absorbent charcoal filling, it has been of outstanding utility in the progress of low temperature research. The picture has only been sketched in briefest outline : how few would at first thought connect the airship, the electric lamp, the picnic flask, and the Sunday joint with Faraday's attempts to liquefy gases. How pregnant for the future may be the researches that are being made to-day by the contributors to this volume.

It is not enough to produce cold and maintain it within the insulated walls of a chamber, to bring meat, fish and fruits unchanged to our table. Attention has to be paid to many other factors, some of them of considerable complexity and involving all branches of chemical knowledge. It is satisfactory to note that a special Low Temperature Research Station has been

equipped at Cambridge, by the Department of Scientific and Industrial Research, to study the chemical changes which take place during cold storage and ripening, and other low temperature problems.

It is only within the present century that real progress has been made in the knowledge of foodstuffs. It had been realised that in addition to small quantities of mineral salts the body required a certain ratio of carbohydrate, fat and protein food to maintain it in health, and it was customary to express these quantities on an energy basis in terms of calories. This was the basis of rationing during the War. Although the result was not unfavourable, the value of quality in food as opposed to quantity was also gradually brought home to a good many sceptics. Some years previously the possible differences in the food values of the proteins, owing to their being built up of different amino acids, had been emphasised and there is now reason to think that fats are not all equally available. There is still much to be done in this field in studying the effect of specific units, but so long as we enjoy a mixed diet the problem is not of pressing economic importance; interest in it for the moment has been superseded by a discovery of outstanding interest and importance. It was found by Hopkins, whose name is associated with most of the really effective steps forward in the domain of biochemistry of late years, that whereas animals could be kept in a healthy state and even grew on a natural food, as, for example, milk, they invariably languished or died when fed with an artificial mixture of fats, proteins, carbohydrates and minerals of the same composition as the milk. Even this diet could be rendered complete by the addition of a very small amount of fresh milk. It has been proved beyond question that in many foods accessory factors exist and that their presence is absolutely necessary in any diet on which an animal can develop normally. These substances are termed vitamins: they appear to act as stimulants or catalysts, and not to contain some necessary complex substance which the animal body is unable to manufacture. Fuller investigation has shown that there are at least three or four of these vitamins—one of them is associated with fat, and its absence from the diet is at least in part responsible for such maladies as rickets. Another is found in yeast and in seeds—its absence from the food in Eastern countries has been held to cause beri-beri. A third is the antiscorbutic vitamin which occurs in green vegetables and fruits. The discovery of these vitamins has thrown much light on many maladies associated with malnutrition, and their presence or absence forms an important criterion of foods—so far there is not the very slightest clue to their chemical structure or indeed to the nature of their action, and recent observations of McCarrison in India would lead us to pause before being too absolute in our conclusions as to their activity and importance. The proposition is perhaps far more complex than has been supposed. However, a new conception has been introduced into the study of food materials, that of stimulation: a similar explanation has latterly been given in connection with the function of certain of the ductless glands, which secrete well-defined substances capable of acting as chemical messengers. We are learning that the control of the body functions is in part chemical and in part effected through the nervous system.

When the achievements of the engineer, particularly in connection with the use of steel and new alloys in constructional work, are acclaimed, it is easy to overlook the assistance rendered by the chemist in the field of metallurgy. The study of steel, not only by chemical analysis, but also by the more refined technique of the microscopist, has given an enormous impetus to the proper understanding of its properties and the influence exerted by small quantities of other substances. The names of Sorby, Stead, Arnold, and other pioneers in this field will long be honoured. Stead, in particular, was one of the first in Britain to grasp the importance of Sorby's

investigations with the microscope, which have led to metallography being made a science. The result has been that the microscope is now systematically applied to the study of the crystallisation phenomena, not only in iron and steel, but also to metals generally. Dr. Desch gives some idea of how far the work in this field has taken us both in theory and in its practical applications.

One further illustration may serve to show the manifold activities of the chemist—namely, the problem of liquid fuel. Mineral oil as obtained from the earth was used originally only for direct burning or when refined for lubrication; the advent of the motor-car created a demand for light oils of low boiling point which had previously been of little value; to-day this class of fuel is the main product of the industry. The demand would probably have already outstripped the supply but for the success of the chemist in inventing cracking processes whereby heavy oils are converted with a minimum of loss into petrol. But there are signs that the oil fields of the world, including any new ones which may come into production, will not be able to cope with the growth of the internal combustion motor, and the chemist has for years been hard at work to find alternative sources of liquid fuel. Through the improvement of the process of distilling coal it has been made to yield large additional quantities of benzol and, on the other hand, much attention is being paid to methods of low temperature carbonisation with a view to the direct production of oil fuels.

Even more attention is being paid to the only other possible substitute for petrol, namely, alcohol. Alcohol is at present so important a source of revenue both in this and many other countries that its production is safeguarded by restrictions almost to the extinction of the industry when it is desired to use alcohol for other than potable purposes. Much work is, however, being done both to produce it cheaply and to alter the internal combustion engine so as to use it. Under the Pure Methylated Spirits Regulations of 1921, alcohol is now being denatured and used for motor transport in this country. On the Continent, its synthesis by catalytic processes from acetylene attained considerable importance during the War, the cost depending on cheap electric power and on satisfactory yields being obtained in a series of difficult reactions. More probable processes are based on fermentation of cheap or waste carbohydrate materials, probably after a preliminary degradation to sugar (glucose) either by chemical or fermentative agencies, the amylo process being one of the most promising. It may well be preferable to carry out such processes in the Colonies, where ample sunlight and high temperature mean quick production of carbohydrate. There is little doubt that the problem of the cheap production of alcohol is on the point of being solved.

To many of us the real goal of the efforts of the chemist is to acquire such intimate knowledge of the structure, properties and behaviour of his compounds that he may at last gain an inkling of the mysteries of nature. Progress in this direction is already becoming rapid now that our investigation of the great natural groups of substances, the proteins, the fats and the sugars, has attained a considerable degree of exactitude.

The substances classed as the sugars or carbohydrates are unique among chemical substances on account of the high proportion of oxygen in their molecule and the number of asymmetric carbon atoms they contain. In consequence, there are no fewer than sixteen distinct isomerides of glucose, and a legion more if closed ring formulæ be taken into account; there are still more substances of the same ultimate composition of a ketonic structure. The unravelling of the mysteries of this group, the synthesis of its members, and the proof of their constitution rank

perhaps as the most wonderful achievements in organic chemistry. Carbohydrates are the main constituents of the plant and form the bulk of our food, whilst their importance in what may be termed the more subtle points in animal metabolism is only just beginning to be appreciated. Nowhere else does Nature ring so many changes on what might at first be called a simple theme, and no chemist can help a feeling of awe, of mystification, at the intricacies of the sugar molecule. These subtle changes in structure have a biological significance, as they serve to decide whether or not a particular material shall take part in the ordinary metabolism which is brought about by agencies known as enzymes, described by Dr. Harden in his chapter on Fermentation. Slight variations in the structure of the molecule thus serve as a regulating mechanism for the vital functions. The chemist has learnt much from the systematic study of the sugar group, in particular as to the relation between optical rotatory power and structure and the mechanism of the reversible changes into one another which closely related forms undergo. Curiously enough, the actual structure of cane-sugar itself is still a matter of controversy, and its synthesis is not yet within our reach. The nature of starch and cellulose for a long time eluded investigators, but, to-day, a very fair idea has been gained of their basic or nucleus structure, though it remains to extend this to the large colloid molecules which we know in practice. Both materials form the basis of a multitude of industries, and their properties in the aggregate are exhaustively known : it is a striking comment on the difficulty of the subject that only now are we learning their real structure, though, in explanation, possibly something might also be said as to the neglect of research in pure science by industry. Mr. Cross's chapter on cellulose must be read with the understanding, based on sympathy and knowledge, which it requires before the full merit of the achievements which he outlines can be appreciated. A veritable magician, the chemist has wrought his spells to charm wood into silk, leather, explosives, and what not more.

The fats, curiously enough, are unfashionable in chemical circles, though their importance in industry was never greater. This is perhaps because it appears, at first sight, that their investigation is mainly a problem for the organic manipulator—a type of worker which, alas ! is fast becoming extinct—and yet the problems in fat chemistry, as Mr. Allan shows, are many. The demand for fats, other than butter fat, for food purposes has become enormous, and has led to great developments in the industries—now largely British—based on the winning of vegetable oils from nuts and seeds. The quantity required for the soap and other industries also continues to increase, though this has been in part met by the discovery how to reduce liquid unsaturated fats, on the large scale with hydrogen in presence of a catalyst, so as to obtain saturated solid products. Whilst the structure of the more common fatty acids is established, much remains to be done in investigating the form in which they occur as mixed glycerides and which gives to each fat the special qualities which are associated with it and are of technical importance. We have very little knowledge as to how fats are built up in the plant and animal, and, conversely, how they are used up.

Five and twenty years ago our knowledge of the nitrogenous constituents of the cell was small, but the progress since has been amazing, and Dr. Plimmer's chapter shows how full and varied to-day's information is. The great protein molecules are made up of a limited number of different but closely allied simple molecules, so that the differences between the proteins is to be explained on the basis of variations in the arrangement and proportion of these units, an almost infinite number of varieties being theoretically possible. Nitrogen in such compounds is far from being the inert element which we picture in our atmosphere, and the forms in which it exists in combination afford infinite scope for a multitude of chemical actions.

The obvious question arises as to how far the chemical composition of any individual organism is constant in regard to the particular special forms of protein fat or carbohydrate it contains or elaborates at particular stages in its life-history. It appears possible to answer to-day that the outward differences which biological systematists observe and use as the basis of classification into species are always accompanied by inward chemical changes, so that we may expect a chemical classification of species in the future and regard as proven the inheritance of chemical factors including chemical idiosyncrasies. It is too early yet to say what is the precise function of the various special chemical compounds in the plant, for example the glucosides; as to the universal constituents it is clear that each species has elaborated a special chemical edifice for itself, specific both in detail and in its finality as judged by outward characteristics. Each of us differs from our neighbour as the result of a difference in the structure of the molecules of which we are composed—molecules composed of the same elements but differently arranged.

Thus, for example, the patient work of Osborne and others on the proteins in seeds has shown that similar proteins are only present in seeds which are closely related. Proteins from different seeds vary noticeably from one another, whereas the fatty acid and carbohydrate constituents are practically the same in all seeds. Such differences in the reserve food substances of the seeds must have an important bearing on the development of the embryo which derives its first food from them. This food substance, as well as the tissues of the embryo itself, are the final products of the metabolism of the plant which produced them. When the embryo first develops it is supplied with a definite food which, for each individual of the same species, is the same but for those of different species is different. Each member of a species thus begins its individual life under similar chemical conditions, but subject to variations which are different from those of every other species. It seems probable, therefore, that when the plant has reached a stage of development at which its organs of assimilation are able to furnish it with nutriment from its external surroundings, its chemical processes have already been established along definite lines which it must follow throughout the rest of its life.

Our introduction is finished: as Robert Louis Stevenson has said:

"To travel hopefully is better than to arrive and the true success is labour."

THE RÔLE OF CHEMISTRY IN PHYSICAL SCIENCE

By Professor Irvine Masson, D.Sc.

A. Introduction

The aim of this chapter is to convey a view of the place of chemistry in science, and to show enough of its modes of discovery to enable a layman to form a general idea of how a chemist thinks, and where his work leads him in the present century.

Whether the investigator bears the label "chemist," "physicist," "botanist"—whatever his peculiar 'ology—only one broad way is legitimately open to him. That way is, first to observe and to record; secondly, to classify accordingly; then, and only then, to speculate; any hypothesis so formed is now tested, first by discovering what it logically implies, and, next, by comparing all the implications with the facts, already known and freshly sought.

There are, then, five successive processes. Of these, some appeal especially to one race or to one type of mind, some to another; genius, as distinct from patience and care, perhaps makes *most* difference when it is used in the middle three stages, and can flash through any of them so as to seem to leap it altogether; yet, whether the five are performed by one man or by many, at one time or during years, *all* of them are necessary to establish that which natural science seeks to find out. And the rightness of an interpretation is altogether dependent upon how far it continues to withstand the assaults of the last process of them all: the test of further observation and experiment.

The youth of a science which uses this method is marked by being *qualitative*. For example, consider these types of statement: iron is magnetic, water is volatile, indigo is dark blue, alcohol heated with sulphuric acid forms ether; these are all *qualitative* statements of what has been observed. Obviously, a systematic course of discovery along such lines yields results of the highest importance, and no progress whatever could be made without this type of investigation. At an early stage in chemistry, however, still earlier in physics, and lately in biology, it was realised that the qualitative method alone has its limits, and that the scrutiny must be intensified. Nature works by strictly-measured quantities, whether of matter or of energy; and a knowledge of such quantities becomes essential for adequate understanding. It is *not* the abstract quantities themselves which are interesting, but the concrete picture which our measurements of them enable us to form.

Thus, while qualitative discovery in chemistry continued and, happily, still continues, "physical chemistry" arose; it is simply the *quantitative* study of the inherent properties of substances, and of their reactions towards each other and towards the various forms of energy.

If this definition be criticised as too wide, since it seems to include most of physics as well as chemistry, the answer is, that the distinction implied by the criticism is out of date in this twentieth century. There are many kinds of physicists, many kinds of chemists, but there is only one Physical Science, for which they both work; and perhaps the outstanding intellectual achievement of our time is that which enables such a statement to be upheld. In order, then, that we may place in due perspective the value of progress in any one branch of Physical Science, we must first have a clear vision of the whole, and must express in concrete terms the single end towards which our diverse endeavours now drive.

The desire to find the Units, whose assembly and interplay shall express things as we know them, is a mental necessity and an instinct in any human enquiry. It is the satisfaction of this desire which is the real goal of the worker in pure science; he is a creature whose hope is, not to

spoil, but to help to reveal the beauty of the scheme of things, and to portray the tangible unities and the rhythms which rise clear from the seeming complexity of nature.

The foremost aim, then, of physical science to-day may be taken as the discovery of a fundamental unit of matter; of a fundamental unit (if there be one) of action or energy; and, ultimately, of the cause-and-effect connection between these two units. Although we do not at all presume to determine the deeper explorations of the future, it seems justifiable for us now to say that the first of these units is nearly in our grasp, the second is apparently drawing within range; but the definite capture of both involves that of the third, which is no nearer than the horizon.

When these three questions have received their first assured answers, there will be still further probings of the infinitesimal, till the bounds of reality are touched; but the vast bulk of investigation will be increasingly occupied with what physics and chemistry are already beginning to attempt, namely, with the task of learning how to use the three answers; how in terms of them first to translate and next to predict—verifiably—the behaviour of the progressively larger units, without whose prior discovery any reply to the three questions must have been vain and without foundation.

It will be in the course of the spread of this new three-letter alphabet, just as it is during the present working-out of the 92-letter alphabet of the atoms, that those discoveries accrue which invention will use for increasing human prosperity.

The distinction drawn between discovery and invention is a real one. The march of pure knowledge in its many groups has been likened to the advance of allied armies, each sending forward its skirmishers, each busy in extending its front, in establishing contact with others, and in consolidating ground already won. And the useful application of that knowledge, under the control of "*meum* and *tuum*, that great Rudder of humane affairs," is like the civil occupation which follows the army. It is to be noted that the progress of the civil occupation is limited by that of the army; and that an army marches on its stomach, even though it fights with its brains.

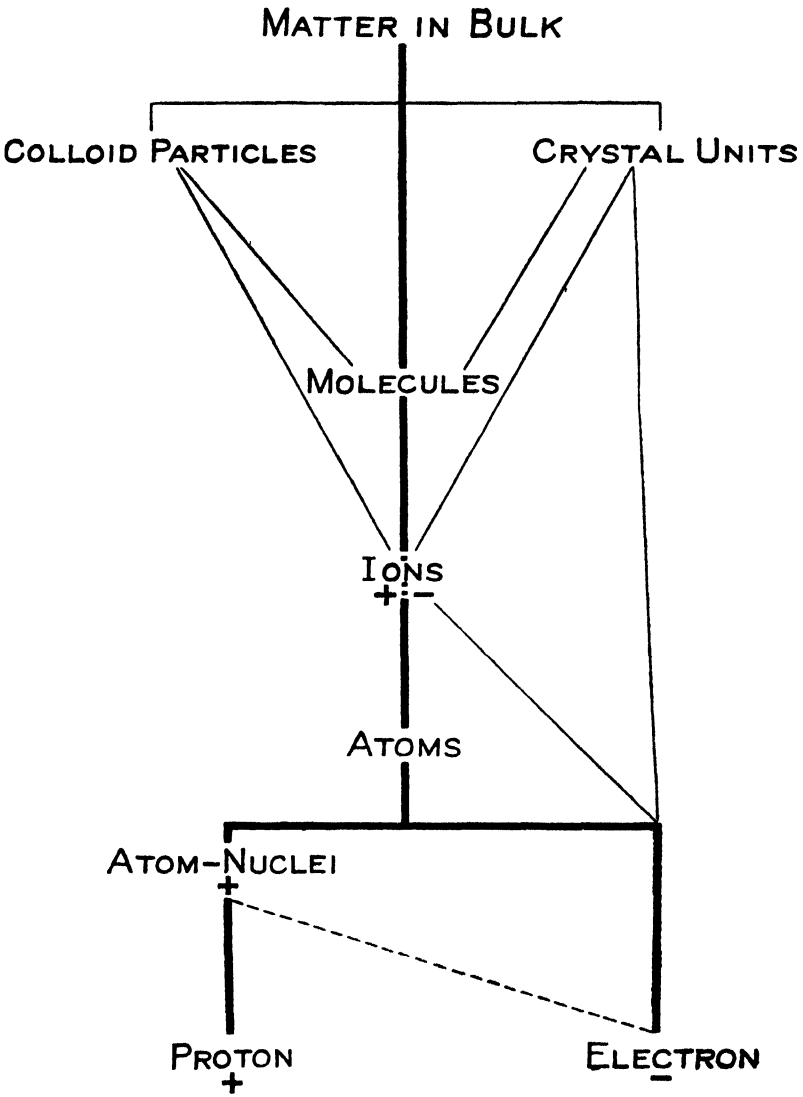
Before summing up, let us recall that the kinds of energy and of matter which we know are not merely terrestrial but are universal; and we owe this truly mighty knowledge to the genius of Newton and to Kirchhoff's work with Newton's spectrum.

Now to sum up. To express the units of our stellar universe in terms of unit masses which we can see and weigh and handle; to express, these, in turn, in terms of molecules, molecules in terms of atoms, and atoms in terms of protons and electrons, and thus by steps to link the great with the small: these are actual themes of research to-day. In the domain of energy, the interconversion of some of the forms has been described by the principles of thermodynamics, a subject which now bears to physical science much the same relation as geometry bears to geography; and a unitary conception of radiant energy, the "quantum theory," is being rapidly developed and put to the test.

With this general introduction, we may go on to review, in a very broad fashion, the part which is played by chemistry, remembering that the particular units revealed by this branch, and in especial by that mode of it called physical chemistry, are the molecule, the atom, and the ion.

It will be seen in the course of the story that the ion (hitherto not mentioned) is one of the

earliest units which have proved to be expressible in terms of the more primitive varieties. There is, further, another unit, which will be barely touched upon: the colloid particle, which is dealt with at large in another chapter. This is one of the two units which link molecules and ions with matter in bulk, the other intermediate object being the "crystal unit." Existent



in liquids chiefly, the colloid particle is also represented in gases by mist and by dust. It owes its peculiar properties to a special arrangement of the molecules which ensheathe it; so that it crudely reminds us of organised bodies. It is, indeed, a link not simply to matter-in-bulk, but is especially significant, and is mentioned in this place, because it forms a bridge between the small units of physical science and the cells and micro-organisms which are the units of biology.

Through its introduction, biology is becoming one of the affiliated branches of physical science, at least in so far as it is now seeking to learn which of the properties of living matter are also those of inanimate matter.

The scope of physical science, as far as concerns the units of the fabric of matter with which it has to deal, but neglecting the interwoven themes of energy, may for clarity be shown by the foregoing diagram of the great analysis which is being made.

In the sequel, we shall by no means confine ourselves to work of the past twenty-four years; for the twentieth century has brought to a head so many lines of investigation that it can be properly viewed only in relation to the nineteenth. The eighteenth century and the second half of the seventeenth (when Boyle launched chemistry as a science) were the pre-unit period of pure observation and classification.

B. The Molecule

I. The Physical Molecule.—When cold water dries up by evaporating into vapour, it expands itself nearly forty-thousandfold, and this vapour can be expanded still more, without any definite limit; and it can intermingle with air or other vapours to any extent. We find it impossible to conceive of a *continuous* material which could be endowed with such properties, and we are compelled, in the face of these facts, to assign to water, and to everything else which shares such properties, a "discrete" structure; that is to say, to picture it as being made of separate little masses which can spread far apart or can aggregate. These *molecules* must be very small, for no microscope will show them. A gas or a vapour, then, is pictured as being mostly empty, weightless space (whatever "empty" space is), with here and there pin-point massive molecules in it. In a liquid, the molecules would be quite close together; in a frozen solid, they would presumably be nearly touching, and (in a crystal) massed in orderly ranks and piles.

Yet this is not all; for, despite the tenuous structure thus attributed to a vapour or gas, it has very definite powers of resistance, as everyone knows who pumps a tyre. By cooling the gas, it is made to shrink. The question thus is necessary: What is there which could keep the molecules apart, especially at higher temperatures? They might be thought—and have been thought—to exert upon each other at a distance some force of repulsion, whose strength increases when the gas is made hotter. This idea must not be lost sight of; nevertheless, it entails the invention of a novel agency, for whose existence there is no other evidence; and consequently, in accordance with the plain logic of common sense, we must first see whether some more familiar agency will not fit the facts.

We therefore try the suggestion that these molecules, not necessarily repelling each other at all, are in motion in all directions, as with a swarm of flies in a room. Each of our "flies," however, since from the outset we deny it free-will, must be presumed to dart on without turning, until it collides with others or with the walls of the vessel. What must be its fate after collision? Obviously, if it then stopped altogether—if the insects flew about in a room lined with a sticky fly-paper instead of wall-paper—the gas, as such, would in the course of time disappear from the middle of the vessel; but it does not, however long it is kept. Hence if there is molecular motion at all, it must be elastic motion; the molecule when it hits anything must bounce off and resume its flight, and so on unceasingly. No doubt, at any moment, some

of the molecules are moving slowly, some quickly, retarded and accelerated by their own encounters; but there could be stated some average degree of speed or energy of movement.

Now this conception—the "Kinetic" conception—is useful in two ways to begin with. It enables us to visualise the mechanism of gas-pressure, which we picture as due to the steady drumming of a hail of molecules on the walls of the vessel. And it enables us to visualise the mechanism of temperature and the conduction of heat; for, whether the body be gaseous or not, it is easy to grasp the notion that the hotter it is—the more heat-energy it contains—the greater is the average energy of the molecular movements within it. Conduction of heat from one side of a body to the other is simply the communication of a more energetic motion from each molecule to the next in front of it, by means of the collisions and impulsions which occur. That is partly why solids are better conductors than gases, for in them the molecules are closer and so collisions are more certain; and that is also why a "thermos" flask, from whose hollow walls all air has been extracted, will let practically no heat get in from outside nor out from inside, except by the narrow avenue of the solid neck.

All this "kinetic hypothesis" can be put in a precise and mathematical way. So expressed, it was found to imply, as exact and necessary deductions, *all* those actual facts of gaseous behaviour which are summarised in the experimental laws of Boyle and Charles and Dalton and Graham. It was also successful in expressing a great deal of other work, when it was used in conjunction with the principles of thermodynamics, which themselves involve no sort of assumption whatever as to the inner structure of matter. On the same purely physical grounds, it was even possible to infer that some gases are composed of molecules which must be in some way complex structures; to maintain the inward throbbings of which, a part of the heat supplied to the gas is automatically diverted. What these structures are, chemistry had already been called in to decide.

We therefore now hark back, to trace the other road which led up to this point.

II. **The Chemical Molecule.**—At the beginning of last century, Dalton, studying the relative weights in which pure substances unite together chemically, discovered that for chemical purposes each of the sorts of elementary matter is made up in characteristic bundles, whose relative weights, not necessarily the same for all elements, can be ascertained by measuring the combining proportions of weighable samples of the elements. These bundles, said Dalton, must be simply multiples of characteristic atoms.

The atomic theory, now for the first time put forward in a form amenable to experimental test, gave to chemistry the status of a unified science; great numbers of known facts became linked, and the accumulated knowledge of a century and a half, founded on the labours of Boyle, Mayow, Black, Scheele, Priestley, Cavendish, and Lavoisier, was ready to be knitted into a single structure.

Yet, before uniformity could be properly achieved, and while the immediate indications of the atomic theory were being explored, it became necessary to clarify the concept still further; and naturally, this demanded still more experiments. For, as yet, the connection between these atoms and the larger units of which they are the parts was not sufficiently clear; the kinetic molecular hypothesis was not to be framed till long after. Gay-Lussac, measuring the proportions in which gases will combine chemically, found that the volumes of the combining gases are always extraordinarily simply related. It was Avogadro who pointed out that the only sensible interpretation of this is, that a given volume of any gas consists of a number of particles, *which number does not in the least depend on what sort of particles they are.* Thus, in

forming water, 2 litres of hydrogen are found to join with 1 litre of oxygen, and this is simply a manifold repetition of vast numbers of unions, each of which occurs between 2 ultimate particles or molecules of hydrogen and 1 molecule of oxygen. When, moreover, it was found that the volume of steam formed from one measure of oxygen is just two measures, it followed that out of every single molecule of oxygen there had been formed two identical molecules of water. That is, the molecule of oxygen had been split into two, each half going with a whole hydrogen molecule to form a whole molecule of water. These two halves are the chemical atoms of oxygen, whose molecule is built of them.

It was the fusion of the molecular hypothesis of Avogadro with the atomic theory of Dalton which supplied a really firm basis for chemistry and rescued it from a condition of unhappy entanglements. Curiously enough, although Avogadro's hypothesis was put forward within three years of Dalton's, that fusion was not effected until nearly fifty years afterwards, in 1858, at the hands of Cannizzaro. The chemical results will be indicated in a later section; meanwhile, it can be said that they were so far-reaching, and in themselves carried conviction to such a degree, as to fortify almost to the point of impregnability the two theories from which they depended and which at the same time they more richly expressed.

At about the same time as this began to take place, the kinetic theory outlined in our initial paragraphs took shape, in the hands of Clausius and Clerk-Maxwell. As we have seen, it was at once fully successful in explaining the then-known facts of the physical properties of gases; but it did more, for the physical kinetic theory was shown necessarily to imply the hypothesis which Avogadro had promulgated on chemical grounds. Thus, gaseous physics and the whole of chemistry could now rely upon each other's full experimental support in their joint conception of the molecular unit, which could henceforth be called the physico-chemical molecule.

We may for clearness describe the later work on the molecule in two sections, which, strictly speaking, overlap in point of time, and bring us up to the present day. Much must be omitted, or barely mentioned; and nothing like justice can be done to the skill and courage of the experimenters; all one may hope to convey is a little of their logic and its results.

III. Weighing and Counting Molecules.—(*a*) *Relatively.*—With the advent of Avogadro's hypothesis, it became possible to find by experiment how many times heavier a single molecule of one gas is than that of another. If we were to weigh two heaps of coins, one heap of florins and one of halfpennies, and we found, let us say, that the florin-heap weighed 2·1 times as much as the halfpence-heap, this alone would not allow us to say how heavy one florin is when compared with one halfpenny. But if we were then told that there had been the *same number* of coins in each heap, then (without having to know what that number actually was) we should at once say, one florin is 2·1 times as heavy as one halfpenny. So it is with gases; for Avogadro shows us that we do get equal numbers of molecules to weigh, if we choose equal volumes of our gases (at some one fixed pressure and temperature).

In this way, the molecular weights—that is to say, relative molecular weights—of different substances are measurable. When, in addition, chemical measurements have shown what elements, in what proportions, are present in these substances and therefore in their molecules, we can say how much the constituent elementary atoms of a single molecule weigh. It is all *relative* so far; for instance, the molecule of water is nine times as heavy as the molecule of hydrogen, and in both of them there is twice as much hydrogen as the smallest amount of hydrogen found in any other molecule. This least quantity defines the atom of hydrogen, H; and because it is the lightest atom known, its weight may be provisionally called 1, until we

know its weight in ordinary units. To the chemist, the symbol " H " does not mean simply the substance hydrogen; it means one atom of it, weighing 1. Hydrogen gas is made of molecules each of which we write " H_2 "; the water molecule, containing this quantity and one atom of oxygen, is the object symbolised by H_2O. These symbols show *amounts*, then, just as much as 2*s*. 1*d*. does; in fact, there is no particular reason why we should not write this molecule of money as S_2D. We have in the foregoing a very short summary of that fusion of Avogadro's hypothesis with Dalton's which has already been mentioned.

The experimental methods for finding the relative weights of gases are very simple in principle, but not so easy in practice; for the gases are naturally very light compared with the vessels in which they must be weighed, and any small errors in the accuracy of the weighings therefore bulk largely. Morley in America, the late Lord Rayleigh, Guye at Geneva, Whytlaw-Gray here, have in turn developed the methods so that with ordinary gases, such as oxygen, nitrogen, nitric oxide, and the like, we can now trust some of the relative gaseous densities as being accurate within two or three parts in ten thousand. Methods have also been developed so that, where a substance becomes gaseous only when strongly heated, it can then still be weighed, indirectly; and such methods have been used up to 2000° C. An interesting example (at ordinary temperatures) was when, with exceeding skill, the late Sir William Ramsay and Dr. Gray used the micro-balance of Steele and Grant to weigh the gas niton or radium emanation; the quantity available weighed one-thousandth of a milligram, and its volume was about a tenth of the size of an ordinary pin's head.

(*b*).—The next step towards counting molecules was made in a great expansion of work, which enabled the operations of molecules to be traced elsewhere than in gases—hitherto the only physical state of matter in which this could be done with any certainty. It was, of course, recognised that molecules are everywhere present, in liquid solutions as well as in gases or anywhere else; but the advance consisted in the proof that the dissolved molecules in *solutions* confer upon those liquids a group of properties which enables the relative numbers or weights of these molecules to be counted, as if they were molecules in a gas. For example, the tendency of water to evaporate into vapour, and its tendency to freeze into ice, are found to be lessened when a foreign body is dissolved in it. The solution has to be made hotter to boil it and colder to freeze it, compared with pure water. Again, pure water tends to diffuse, molecule by molecule, into a watery solution, if this is placed in contact with it in such a way that ordinary rough mixing does not occur. The fewer the water-molecules in the solution—that is, the more numerous the foreign molecules—the greater is this tendency; and if the swelling of the solution by interpenetration of the water is to be prevented, mechanical pressure—known in this connection as " osmotic " pressure—has to be exerted on the solution. All these properties of solutions, then, can be measured and exactly expressed; and in a great mass of diverse work which was brought together by van't Hoff at Leiden in 1887, it was shown that one and all depend upon the *numbers*, not at all on the *kinds*, of the foreign dissolved particles in the liquid. We are forcibly reminded of Avogadro's and the kinetic theory of gases; and evidently here likewise is a means of relatively weighing or numbering dissolved particles.

One outcome of this was to be the discovery of ions, told in a later section; the other which now concerns us is as follows: for clearness it is told in a very much simplified form.

(*c*) *Absolute Counting.*—It has been found that the foregoing " osmotic " effects are shown, not only by solutions, but by *suspensions* of visible particles in otherwise pure water. In this

case it is possible to count the foreign particles by eye, assisted with the microscope and, better still, with the ultra-microscope; and it turns out that the " osmotic " effects depend, once more, on the *number* of the suspended particles, in exactly the same way as with dissolved molecules and with gaseous molecules. It is these suspended particles which are the colloid particles referred to in the introduction.

By these physical tests, then, visible mud-particles *are* molecules; and, since they can be counted by eye, we are provided with a means of finding the real number, not merely the relative number, of molecules in any gas.

Actually, the molecular nature of suspended particles is even more convincingly shown; for they can be seen to be in motion, hither and thither, in the fluid. This long-known " Brownian " motion has been timed and measured by various means, including the use of the kinematograph; and it turns out to be precisely that which, on the kinetic theory, would be given by magnified molecules having the size and weight of these particles, moving through a liquid, and bombarded by the (invisible) agitations of the liquid's own molecules. One might say that as a result of this twentieth-century work, the presence of the liquid's own molecules, and their movement, have been proved to be as real as the dark stars; and we are as firmly assured of the true existence of molecules in general as an astronomer would be assured that Mars is really a world, if he paid it a visit in person.

Measurements of this sort have been confirmed by a large number of investigations of other kinds. Some of these, as in Rankine's experiments upon gaseous viscosity, are made with materials in the ordinary molecular condition of gases; others, as in the researches of H. A. Wilson and of Millikan upon the movements of electrified mist-droplets, have had to do with aërial colloid particles and with electrical measurements. All the results converge upon the same conclusion, so that we now know with very fair precision the actual numbers and the approximate sizes of molecules.

In a drop of water there are some two thousand million million million molecules. This conveys no conceivable idea; so we may put it in another way. Supposing that we were to magnify one drop of water to the size of the earth, and all its molecules and their atoms proportionally, we should see a space populated by something like trios of toy-balloons, bouncing about everywhere at intervals of no more than two or three feet.

That it has been possible to prove anything at all, let alone to prove anything precise, about objects so minute as molecules is no doubt wonderful enough; but the real miracle is the molecule, not our methods of divining it. The thing is so small, and yet it decides the behaviour of bodies so great, that it lies far beyond the limits of insignificance and, rightly considered, is awe-inspiring; and still more so when it is realised as being formed from things even smaller.

IV. **Molecular Attractions.**—(*a*) *The Liquefaction of Gases.*—The obvious fact that some gases are more easily liquefied than others—for example, compare steam with air—shows that some molecules tend to cling to their kind and form aggregates. No gas known at the present day has resisted liquefaction. Many gases, such as laughing gas, carbonic acid gas, and others, can be liquefied without cooling them, by simple compression. Others, the " permanent gases," like air, hydrogen, and so forth, have been compressed up to 20,000 atmospheres—100 to 150 tons per square inch—without showing any sign on the way that there was any separation of liquid, though the very molecules were compressed and distorted. But even these gases liquefy by pressure, provided that they can first be cooled sufficiently.

It was Andrews, in Belfast, who in the 'sixties first showed what he called the " continuity

of the liquid and gaseous states," and demonstrated the existence of a " critical temperature " for each gas, below which it can be liquefied by pressure, above which it exists in only one form, more or less dense. One-half of the principle of the liquid-air machine is that whereby the air must not only be compressed, but must be compressed when it is below —140° C.

Van der Waals next showed, by a modification of the kinetic theory, that the existence of a critical temperature, and, in general, the new facts which Andrews and his successors discovered, can be accounted for by allowing for two things, neglected in the simple theory, namely, that molecules have size, and that they tend to stick together when they are close. This " cohesion " works, of course, against the independent motion which tends to keep them apart. It is not quite the same as the force which makes one atom combine with another chemically; at all events, we find cohesion even among the gases of the argon group, and the atoms of these are not known to form any chemical compounds at all. Although various ideas are current as to what might be the origin of molecular cohesion in gases and liquids, they are still under test. No sort of explanation of cohesion is therefore justifiable here; we shall accept the fact and leave it at that.

We may note at this point one or two uses which are made of this cohesion. Evidently molecules can cling together with a good deal of energy; and correspondingly, it requires the using-up of a good deal of energy to draw them apart again. When a compressed gas which contains cohering molecules is suddenly released so as to expand, its molecules are compulsorily drawn apart; and the resulting using-up of energy, necessary to provide for this separation, makes the whole gas cold. The liquid air machine makes use of this method of chilling, in order to bring the air to the pitch of cold at which it can begin to liquefy—its critical point. With the help of liquid air which is boiling away in its vessel at —200° C., even hydrogen can be cooled enough to make it liquefiable; and with the aid of liquid hydrogen, the most " permanent " gas of all—helium—has been liquefied by Kamerlingh Onnes at Leiden. Onnes has used this liquid helium to obtain the lowest temperatures ever known; he has reached within one degree of the absolute zero of cold, —273° C. At such a temperature, " 1° Absolute," everything except helium is rigidly solid; and the molecules are all but lifeless. It is not improbable, from what we otherwise know of its molecules, that helium may prove to be incapable of forming anything nearer to a crystalline solid than a sort of loose-knit and flexible assemblage; but this is a speculation which only those who can test it are properly entitled to make.

(*b*) *Films.*—The foregoing variety of cohesion is not one of whose mechanism we form a very definite picture; but the explanation of it will doubtless turn out to be akin to, if not the same as, that of several better-understood phenomena, which we shall now very imperfectly indicate. Their study belongs mainly to this century.

When a liquid form drops, each of these is held together, and its size is decided, by the tautness of the skin of the drop. This tautness can be exhibited and measured in a number of experimental ways, some of them very delicate in detecting changes in it. The pouring of oil on troubled waters is our most ancient example of an artificial change in " surface-tension." The late Lord Rayleigh studied quantitatively this effect, and measured the least quantity of oil which was necessary to affect the surface tension of water. He showed that the minimum layer is so thin that it seems to be a carpet no thicker than one molecule. Hardy, working by another method, showed that the energy with which films of different oils adhere to the surface of water is definitely connected with the presence of certain atoms or atomic groups within their molecules; and his work, emphatically confirmed by many recent investigators, leaves

little doubt that in such films the molecules are anchored to the liquid or solid surface to which they cling, by reason of forces emanating from certain special atoms in them. Each molecule is, as it were, more sticky at one part than at another; and the whole film on a solid is like a mussel-bed on a rock. Certain of the atoms, though bound to each other within a molecule, can evidently spare some of their force to reach out a little way and attract similarly-disposed atoms in neighbouring molecules; as when a rower reaches a hand to someone on a landing-stage and so makes fast the boatload. We cannot doubt, in the face of this work and of a great deal of strong collateral evidence, both chemical and physical, and too voluminous to be indicated here, that at least a part of molecular cohesion or attraction takes its origin in the incompletely monopolised affinities of one or more atoms within the molecule. It would be premature to push the matter further.

(c) *The Solidification of Liquids.*—It is characteristic of solid crystals that they influence in a peculiar way the passage of light through them. The effect which is well seen with Iceland spar is one example; if a clear crystal of this substance is held at a proper angle and used as a window through which to view, for instance, a ruled line, the line is seen doubled. The effect is called "double refraction." We cannot escape the conclusion that this has to do, somehow, with the *orderliness* of the molecules and atoms in crystals; an arrangement long believed to exist, and precisely shown as a fact by the beautiful researches of Sir W. H. Bragg and Professor W. L. Bragg upon *X*-rays. The total effect produced by a crystal upon a beam of light is thus thought of as the summation of a number of successive small effects, each caused by one small molecule or unit, and all working in the same way because all the molecules or units of the crystal are facing the on-coming beam in the same way.

When the molecules, or such parts of them as bend the light, are higgledy-piggledy, as they are in a gas or a liquid, double refraction is not observed, because on the whole there are at every instant just as many molecules acting in one way as there are molecules acting in the opposite way. The essential thing is, that double refraction implies a preponderance of *order* in the molecular array within the doubly-refracting body. Adopting this test, we may see what it tells.

Gases and liquids show no orderliness. Also a glass shows no optical difference from a liquid; for glasses, and what are called "supercooled liquids" in general, are simply liquids which have been cooled without freezing till they are so viscous as to resist, perhaps for years, any internal settling of their molecules into a symmetrical pattern. As Robert Boyle put it in a flash of insight 264 years ago, "the particles of the Glass agitated by the heat, were surpriz'd by the cold before they could make an end of those motions which were requisite to their disposing themselves into the most durable texture."

Optically, all "amorphous" transparent bodies, such as celluloid, jellies, and colloid "solids" are like glass. Nevertheless, if glass or celluloid be strained mechanically along one direction, then, while the strain lasts, there is double refraction; to some extent the molecules have been forced into lines, rather as if one took a tangled bundle of chains and pulled it out taut. Glass which has not been properly annealed in manufacture is under internal stresses of this kind, due to unequal contractions during cooling, and so is liable to fly in pieces; and the examination for double refraction (by a very sensitive method) is now applied as a routine test of good annealing in many glass-works. Ordinary liquids, too, can show the effect of strain; but since their molecules are more mobile than those in glasses, and are consequently less easily "surpriz'd" before they slip back into random motion, the stress has to be applied rapidly. Thus,

oil which is lubricating two quickly-moving surfaces is found to be in this condition. So also, suspensions of certain rod-shaped particles (iron oxide, vanadium oxide) in water show double refraction if the rods are made to " head " in one direction, either by streaming the liquid rapidly along a tube, or by placing it between the poles of a strong magnet.

Now certain substances have been found which *spontaneously* become doubly-refracting while still in the liquid state. When well above their freezing points, such bodies are quite normal liquids, optically; but as they cool to near their freezing points, they show more and more clearly, under the special illumination used in the test, places of double refraction; and yet any foreign particles which may be present can wander freely through these places, so that these are still liquid. On cooling further, the liquids freeze to ordinary solid crystal masses, retaining and extending their double refraction. It seems from this that " liquid crystals " are places in the liquid where the molecules have begun to string themselves out in anticipation of the array which they will ultimately assume, though in closer formation, in the solid crystal. Evidence of this preliminary " stringing-out " has also been found in liquids which are on the point of forming a fibrous curd.

(*d*) *Change of Solid Form.*—We might have thought that, arrived at the solid crystalline state, the molecules might be finally content; yet it is not always so. To illustrate this fully would require several books; some of the matter is dealt with in another chapter; and we must give but the briefest attention to it.

There are innumerable cases in which one and the same chemical compound or element exists in more than one solid form. The classic example of carbon, in the diamond and in graphite, is only one of many examples of this " allotropy " among the elements. Tin, when it is kept in cold climates, tends to suffer from " tin plague," in which the bright, tenacious metal falls away in pits and patches to a grey powder. The powder is still pure tin; and it has been proved that if this is kept warm it can be made to revert to the ordinary form, though no longer, of course, in a compact shape. Iron has several forms also, and only one of them is magnetic. An interesting compound, ammonium nitrate (the chief component of our war explosives) can change into another and more voluminous form of the same substance so quickly, when kept rather warm, that it breaks the glass vessel which holds it. Hundreds of cases might be cited.

In many of these cases, we can point to a definite temperature of transition or molecular re-arrangement, which is no less definite than the melting-temperature. Often, also, heavy pressure assists in the production and the maintenance of the change; if the form to be produced is less voluminous than the original, pressure inevitably helps. It is most interesting that in the last few years ice has been proved to undergo these changes when suitably compressed. There are no fewer than five " ices," each form with its own distinct properties, and each best fit to exist within its own characteristic range of pressures and temperatures. One kind of ice, which requires pressures of over 40 tons per square inch to form it, exists—and can exist only—at temperatures higher than " freezing-point," *i. e.* over 0° C.; and, under pressures such as 100 tons to the square inch, it has even been kept, perfectly solid, at 75° C., a temperature such as can hardly for a moment be borne by one's hand. The possible bearing of these results upon glacial geology is perhaps worth thinking about; for they limit the pressures and at the same time extend the upper ranges of temperature, at which solid water can exist.

Regarding the nature of the linkage between molecule and molecule in a crystal, we must not invade the province of the writers of the chapter on Crystallography, but we may borrow from them just this: the linking of unit with unit in a molecular crystal is determined, as in

films on surfaces, by stray forces emanating from atoms within the molecules; the crystals cleave or split most readily at the planes where atoms of weak residual affinities are facing each other. An analogy with the splitting of a bread-and-butter sandwich is not as far-fetched as it may seem; for, ultimately, the same forces govern both the solid and the sandwich.

V. A Picture of Molecular Processes.—We may draw this section to a close by describing the intimate mechanism of the passage through the three states of matter which occurs when we cool a vapour. The picture here drawn, it should be remembered, is entirely based on exact numerical measurements, and describes nothing which is not authenticated by them. We begin with the gas enclosed in a vessel of some kind.

The gas is chiefly space, and in this space innumerable molecules constantly fly, collide, and rebound, spin and internally vibrate; if, here and there, pairs and trios are formed, they are instantly dismembered by the onset of molecules whose paths they cross; no molecule is ever at rest for more than a very small part of its perpetual journeying.

As the gas is cooled, the movements diminish in vigour; the transient clusters may form more frequently, last a little longer, and grow a little larger, but within each cluster the loosely tied components are violently vibrating, ready to fall asunder at the first impact. Meanwhile, over the walls of the vessel there has spread a sheathing of molecules, all anchored to those which jut from the solid wall, and serving as targets to others which shoot from the mass of the gas. With further cooling, the coating thickens, as layers of molecules pile up on the first; the clots increase in the gas; and we are at the point when, with a touch more of cold, the clots thicken and merge together from out of the space and, gathering into one loose body, cling to the layers lining the wall: the gas has become a liquid.

All through the liquid, incessant oscillations, jostlings, and slippings-past still go on; and at the cordon of the upper surface, molecules are continually breaking away or piercing the rank to escape into the vapour-space above, and are as continually returning.

As we cool the liquid, the oscillations grow quieter, the mass becomes more compact, fewer molecules break from the surface; more and more frequently, groups of molecules find themselves close enough and suitably set to begin to join in regularly-ordered chains and figures. If at this point we suddenly cool the liquid extremely, the molecules are immobilised where they stand, and in this state of suspended animation they constitute a glass or a jelly; and at a number of points in it there are the groups which await only the release of the constraint to continue the orderly building which they had begun. Allowing the supercooled liquid, then, to grow warm again as it was before the sudden chilling, we regain the state of mobility; and now, with the resumption of gentle cooling, there is reached a temperature where the energy of propulsion can no longer debar the inward atoms of the moving molecules from maintaining their directing drag upon others which come within range of them; all the molecules are pulled into positions of quivering equilibrium, dwelling in serried rows of habitations, and the liquid has frozen into a crystal.

Only by further cooling, and perhaps by pressure, may any rearrangement be made; though this happens with less and less freedom as, with lowered temperature, the quiverings diminish, which perhaps lessens the chance that the right parts of neighbouring molecules shall be favourably placed to bear mutually on one another; but at length, the particles are locked into whatever places are most narrowly and symmetrically fitted to the shapes of their "spheres" of influence. Yet in no case will they cease to vibrate, each within its own confines, until the crystal reaches the unattainable absolute zero of cold.

C. The Atom

For the sake of clearer understanding, we shall diverge from the order of units shown in the diagram on page 25, and shall treat of the atom before the ion.

From the fusion of Dalton's atomic theory with Avogadro's and the kinetic molecular hypotheses (page 28), there came a confidence in the existence of atoms as objects and not as little more than arithmetical counters, which soon won unanimity among chemists. This assurance led, during the second half of last century, to two discoveries, of the highest importance then, and at the present time, in the very forefront of interest. These were: the property of Valence, and the Periodic Classification. Both these subjects receive treatment in other chapters, so that only so much of them need here be said as is necessary for the development of our present theme.

I. **Valence.**—As a result mainly of the study of compounds of carbon by a number of workers, culminating in the researches of Frankland, a new intrinsic and numerical property was discovered in atoms. Hitherto, the measurable properties which had been assigned to atoms had been of a kind shared by any sort of matter; mass, volume, specific heat, are familiar and measurable in bulk-matter, even though we knew nothing of atoms. The new property, however, is characteristic of atoms and of atoms alone; it is the one feature which we might have marked as distinguishing chemistry from everything else, but for the barrenness of any such discrimination.

The valence of an atom is the measure of its capacity to unite with other atoms within a molecule; and the essence of the discovery was that valence is a property which goes *per saltum*, in units. The way was prepared for a simple classification of elements according as their atoms have a valence of 1, 2, 3, and so on up to 8, this being the maximum valence which it was found necessary to invoke.

At first a merely arithmetical property of atoms, valence was later exhibited by Couper and Kekulé, and especially by van't Hoff and Le Bel and their successors, as a geometrical property. For the first time there was produced reason for regarding the atom as something more than a mere lump, and a glimpse was given of its having a characteristic shape; or rather, of a characteristic orientation of the forces emanating from the atom. The story of the development of geometrical valence is told in the chapter dealing with organic chemistry; for it has been the specialised chemistry and the physical properties of the compounds of carbon which have supplied by far the clearest information on this aspect of valence.

Chemical reactions alone, however, cannot afford a knowledge of what actual objects or structures within the atom produce the outflung attractions which link it with others. Sooner or later, the enquiry into these underlying causes was bound to begin; and this became possible when the nature of ions began to be understood, and when the electron had been discovered. How far we still are from finality in the solution of the enquiry may be learnt from the special chapters.

It is worth noticing, before leaving this subject, that another peculiarly atomic property, more complex than valence but much more accurately definable, was discovered at very nearly the same time: the spectrum of an element; and further, that it is the spectroscope which is now proving the most potent weapon in locating the electrons which determine chemical properties, including valence.

II. The Periodic Classification.—(*a*) The newly-certified atomic weights of the 'sixties provided a sequence of numbers whereby all the then-known elements (about 60) could be arranged in order, so that the trend of their properties with rising atomic weights might be examined. An English chemist, Newlands, partly saw and in his "Law of Octaves" in part enunciated the ensuing generalisation, which was fully proclaimed by Mendeléev.

The word "octaves" gives the clue to the nature of the discovery. Just as on the piano we find that with rising pitch we get a periodic recurrence, in due order, of notes so similar as to receive the same names from A to G, so with rising atomic weight, as we pass from element to element, we find a periodic recurrence of similar elements, and all these fall into groups named from I to VIII. Broadly speaking, all the elements within any one group have the same valence, and there is a regular gradation of other properties, from the member with the lightest atom to that with the heaviest; while between one *group* and the next there are all those chemical differences which are associated with the stepwise increase of valence.

The sequences initially suffered from many blemishes; but Mendeléev had formulated, and was confident in, a brilliant hypothesis of rhythm; and he boldly stated that the blemishes were due on the one hand to faulty assumptions made by early experimenters, and on the other to elements as yet undiscovered, for which places should be left vacant in the sequence. From the existing gradations of properties within one group and from one group to the next, he stated in exact figures what the data alleged to be incorrect should be, and he foretold in precise detail what the missing elements and their compounds should be like, both physically and chemically. Reinvestigation of the antiquated data by fresh workers proved him right in that respect; and within 15 years the discovery of two new elements, gallium and germanium, which exactly fulfilled what he had predicted for them, triumphantly vindicated the classification and the doctrine of rhythm.

(*b*) To review all the properties which were "tidied up" and correlated by the Periodic Classification as time went on would be neither possible nor desirable in this place. This systematic study constitutes what is often still called Inorganic Chemistry, although the usual purview of inorganic chemists has by now extended far beyond the stage of simply classifying chemical properties, and has merged almost completely into the scope of general (including physical) chemistry as it is defined in the introductory section of this chapter.

We can only note, then, that the periodic recurrence is seen in such properties of the elements as: metallic and non-metallic nature; ease or difficulty of melting and vaporising; magnetic susceptibility; specific gravity; and among the chemical properties, valence; combustibility; ease of corrosion by various chemical agencies; ionic characters in general; whilst their chemical compounds show periodic changes in physical properties, in solubility, in acidity and alkalinity, and in a great number of other properties, all exactly measurable.

(*c*) What ought to be specially noted here are rather the major factors in the array of the elements, which later work has brought out.

One of these may be expressed by a quite rough analogy with the piano keyboard once more. Just as, in ascending the gamut of notes, we find the simple scale in the key of C major to be invaded by black notes which constitute an excursion from the regular sequence, although each of them bears a relation to one of the white notes in the scale, so also in ascending the gamut of the elementary atoms we come to invasions into the most simple-seeming sequence. The atomic "black notes" are, however, massed together without any alternating "white notes," so that they form a cluster of what are called the sub-groups in the Classification.

Each sub-group echoes to some extent the characteristics of a main group to which it corresponds. It is as if we had to do with what the musician knows as harmonics; and in the chapter on atomic structure it may be seen that this notion is more than merely fanciful, and that we may look forward with some hope to an expression, in terms of the vibratory parts of atoms, of the relations between main and sub-groups, and even of that interesting case of harmonics nearly in unison which the chemist knows as the " rare-earth elements."

(*d*) The second important matter is the discovery of a certain set of elements, which form an entire group of the Classification and whose existence had been quite unforetold. This was the helium–argon group of gases, whose discovery by Sir William Ramsay, with Lord Rayleigh first and with Dr. Travers later, forms one of the most interesting and dramatic stories of chemistry. The reason why no provision had been made for this whole group of substances in the chemical classification became evident after their investigation, for they proved to be devoid of all chemical properties. Yet, now, those elements are absolutely essential to our ideas of why ordinary elements undergo chemical changes at all; for we see in the atoms of the " inert gases " the perfect and completed types, whose forms the atoms of all other elements are automatically seeking to attain when they undergo chemical change. It is by the group of the inert gases that the two chemically-opposite wings of the Periodic Classification are bound together, much as the opposing halves of an arch require a keystone which abuts on them both.

(*e*) Lastly, there is this to observe. In the last 10 years atomic weights have in some degree lost that primary significance, a belief in which first enabled the essential rhythms of the elements to be perceived. Although atomic mass (weight) may yet prove indispensable for probing atomic mechanism, the order of atomic weights in classification has been replaced by the almost parallel, but chemically more definite, Atomic Numbers. The sequence of these was originally laid down on purely chemical grounds; but the epoch-making work of the Cambridge school of physicists has now given to that sequence a character of astonishing meaning and precision. In the light of all that has been done and is being done in the new branch of physical science—sub-atomics—the chemical Periodic Classification remains an indispensable guide, and it presents a crucial problem whose solution is occupying the mathematical physicists of to-day.

D. The Ion

I. The Simple Theory.—(*a*) The fundamental researches of Faraday, which made exact and greatly extended the knowledge obtained by Davy and others, gave the first clue to the way in which matter and electricity are connected. Without adhering to strictly historic sequence, we may review the salient facts.

Pure substances can be put into two classes according as they do or do not allow an electric current to pass through them easily. The really good conductors are all metals; the poor conductors and the insulators are non-metallic elements and most of the pure chemical compounds. The passage of a current through a metal—for instance, in an electric cable—makes no difference at all to the metal; it may grow warm at the time, owing to such resistance as it opposes, but otherwise it remains exactly in its initial state.

When *mixed* substances are studied, we find that there are three groups : one consists mainly of metallic alloys, such as brass, which conduct in just the same way as pure metals, showing

no change thereby; and solutions, on the one hand conducting solutions and on the other non-conducting or insulating solutions.

Taking the two kinds of solutions, it turns out that there are many liquids, like chloroform, petrol, and others, which never yield conducting solutions, no matter what we dissolve in them; others, of which water is the chief, give conducting solutions, but only when the dissolved body is a compound and of a certain wide class of compounds. Thus, solutions of sugar or of alcohol in water do not conduct; those of salts, of acids, of alkalis do. Broadly speaking, those "organic" chemical substances which are not salts, acids, or alkalis are in the former class; all the rest, including the inorganic compounds, form electric conductors when dissolved in water.

We may now confine our attention to the conducting solutions. It is found that they differ profoundly from metals in the way in which they conduct the current; for, whereas metals are unaffected by the passage, these substances cannot conduct except in so far as they are decomposed chemically in the process. Where the current is led into the liquid, and where it leaves, there inevitably appear the separated components of the dissolved compound. Thus, when we pass a continuous current through a solution of copper chloride, metallic copper is deposited at one side, chlorine gas is set free at the other, until all the copper chloride is gone—resolved into its two components. Using ordinary salt—sodium chloride—in solution, a similar thing happens; the sodium all goes towards one pole, the chlorine all goes towards the other; if we do not see metallic sodium as such at the appropriate pole, this is only because this particular metal happens to be unable to exist as such in the presence of water, which chemically attacks it; but its arrival is signalised by the production of hydrogen gas in its place, and the neighbouring part of the liquid is found to be rich in the piled-up sodium hydroxide simultaneously formed. By heating pure salt itself (till it is molten), we have a liquid which avoids this complication, and metallic sodium duly appears at one pole when the current passes.

In this way we can electrolyse, *i.e.* resolve electrically, any member of this class of bodies which is soluble in water or other "conducting solvent" (including the liquids which they themselves form when melted); every one is thus divisible experimentally into two opposite parts or "radicals," which are charged, when in solution, with positive and with negative electricity, according to which electric pole attracts them. Positive radicals turn out always to be the metallic constituents of salts and alkalis, and the hydrogen of acids; the negative radical is what is formed by all the rest of a compound.

Here, then, is a puzzle, over a century old, which requires explaining: Why should the metallic appearance of an element go hand in hand with its being positively electrified when its compounds are dissolved in water or melted? The question will be answered a little later; the puzzle was not solved at all until a few years ago, and is still not perfectly cleared up.

(*b*) The next step is most concisely stated by using the molecular idea, and the atomic theory as it was sketched in the foregoing section. When a dissolved substance is decomposed at a pole in the act of allowing electricity to pass to that pole, it is fairly obvious that molecules must separately be partaking in this process; that is, we are watching on a large scale what is actually occurring to each separate molecule. Each single molecule of the substance, then, is to be thought of as having two parts, one of which is associated with positive electrification, the other with negative; in a molecule such as that of copper chloride, the copper atom becomes positive, and each of its two chlorine partners becomes negative. Arrived at the respective poles, these electrified atoms lose their charges and revert to the elementary state.

It is the electrified atoms or parts of a molecule which are called *ions*.

We thus gain the idea that the act of conduction is one of transport: that the atoms can serve as actual *vehicles* for electricity. What Faraday's experiments did was to show how much electricity the different atoms can carry; and, taking again the single illustration of copper chloride, we may put the result by saying that each of the two chlorine atoms takes one definite quantity of negative electricity, while the single copper atom takes exactly two such quantities of positive electricity. The molecule of copper chloride *as a whole*, $CuCl_2$, like copper chloride in bulk, is electrically neutral.

We have here the first indication of the unit of electricity, which was eventually to turn out to be the electron. Further, it became clear that the number of Faraday units of electricity (+ or −) which an atom can carry or unite with is precisely the same as the number of chemical atoms which it can unite with; to put the matter shortly, its ionic charge is given by its chemical valence. In subsequent chapters it will be seen that this fact is at the basis of our ideas concerning the actual cause of chemical valence, and we must acknowledge Faraday as their founder.

For the present purpose, we have arrived at the view that the electrically neutral molecules of salts, either molten or in certain solutions, can divide into oppositely-electrified atoms or radicals which serve as the vehicles for transporting electricity when a current is turned on. We have still to learn whether the splitting is spontaneous, or whether it is merely local and transient and caused only by the current which is applied: is it inherent in the salts themselves? If we are to answer this we must seek evidence which is independent of electrical experiments; and such evidence we shall now review.

(*c*) In the section dealing with molecules we saw how it is possible to count the number of foreign particles of any kind which are mixed with those of a liquid to form a solution, by means of simple measurements such as those of boiling point or freezing point. These measurements have nothing to do with electrical properties as such.

When this method is applied to solutions in general—whether in water or not—it is found that those solutions which do *not* conduct electricity contain only so many foreign particles as have been put in, in the shape of molecules of dissolved material, when the solution was made up; but that, in the case of conducting solutions, in proportion as the solutions are good conductors, by so much are the foreign particles *more numerous*, than the neutral molecules originally put in. Arrhenius, finding this, pointed out in 1887 the inevitable inference: that the extra number of foreign particles must have been provided by the spontaneous breaking-up of the original molecules at the moment of dissolution; and that, when a current is afterwards switched on, it is these fragments which are alone instrumental in conveying the current. This, then, is the essence of Arrhenius' ionic theory of solution. Uniting the two quite independent lines of work which will always be associated with Faraday and with van't Hoff, Arrhenius proved that Faraday's ions, or charged atoms and radicals, are not merely evanescent aspects of the electrical disruption of a chemical molecule, but are separately-existing though complementary objects, called into existence solely by the intrinsic nature of the parent molecule, and (as far as could then be told) by the medium in which that molecule is placed.

(*d*) A third class of properties was at the same time brought into line; for it was shown that the faculty, peculiarly associated with salts, acids, and alkalis, of undergoing chemical changes instantaneously when mixed in solution, was to be connected with the proved dissociation of the molecules into ions. Further, a number of actions, classed under the heading of

"catalysis" (*q.v.*), wherein the mere presence of one of these compounds is found to hurry on certain slow chemical changes suffered by organic compounds, were shown to be accounted for precisely if the *ions* of the catalysor, and not its unbroken molecules, are the effective accelerators.

II. Later Developments.—In these ways, three great groups of facts were correlated by one theory; and it might be said that for the remainder of the nineteenth century and well on into the twentieth the phrase "physical chemist" meant chiefly one who was deducing or putting to the proof the consequences of the ionic theory. Out of an enormous mass of results we may select two additions which have been made to the simple original theory; these will now be outlined.

(*a*) Arrhenius' own followers did what disciples usually do: they claimed more than he had, and neglected what virtues had lain in older views. But inevitably, the solid facts on which these older views had rested, however insecurely, were revived and enlarged; and now, incorporated in the modern ionic theory of solution, they strengthen it exceedingly.

What was neglected in the first dawn of the theory was the fact that the liquid, in which the dissolved salt "ionises," plays a more than purely physical *rôle;* for, besides acting as a medium which allows the electrified opposites to separate, some of the solvent molecules unite chemically with the dissolved body or its ions. There is a vast literature of experiments and speculation on this, and it is far too technical a matter to enter upon here. All that can be said is, that chemical association with the solvent is inherent in the process of ionisation, and is probably a necessary factor in enabling the electrical charges to be comfortably accommodated upon the ions which are in this way enlarged. In many instances, the union with the solvent happens in a fashion so definite that there is no doubt whatever of its function as a factor which conditions ionisation. Such cases are examples of a general type of chemical union known to chemists as "co-ordination," whose study at the hands of Werner has provided one of the happiest links which have re-united organic with inorganic chemistry, by reason of the methods of investigation and because of the kind of atomic valence which is now found to be operative in the act of co-ordination.

(*b*) The other outcome to be mentioned is more fundamental. It was recognised from the beginning that most salts are incompletely broken up into ions when they are dissolved; and yet there are many properties which are clearly due to ions alone, and which are also manifest in the substance when it is not in solution at all. For instance, the colours of many solid salts are exactly the same as those of solutions in which they are present almost entirely as ions—permanganates, for example. Yet these salts do not conduct electricity when they are solid; if we were to judge by this criterion alone, the solid crystals would have to be described as not ionised.

Here again, the methods of discovery are mainly too recondite to be followed unless one is a regular student of the subject, and once more we must adopt the unsatisfactory procedure of indicating results without adducing the facts which prove them.

Briefly, then, the results are these: those substances which form freely-conducting solutions when they are dissolved are ionised, not only in solution, but also when they are in the pure solid state as well. Thus common salt crystals are made not of molecules of sodium chloride, NaCl, but essentially of sodium ions (Na^+) regularly intermeshed with chlorine ions (Cl^-). The crystal does not conduct electricity, because every ion is rigidly confined, and so none can migrate to carry its charge to the electric poles applied to the sides of the crystal.

When the solid salt is dissolved in water, or melted, or even vaporised at a high temperature, many of these positive and negative ions move apart and become more or less independent, so that they are free to deliver up their electric charges separately at two poles, *i.e.* to carry a current. According to the nature of the intervening medium, the purely electrical attraction of positive for negative—like for unlike—leaves some of the ions as only semi-detached pairs. The difference between "good electrolytes" and "poor electrolytes" lies principally in the degree of this "semi-detachedness" when comparisons are made in similar surroundings; and, as has already been indicated, this degree is markedly influenced by the union which can occur with the molecules of the solvent itself.

The difference between electrolytes in general and non-electrolytes, including organic compounds, is that the latter consist of molecules in which either (i) the positive and negative ions present in the molecule are electrically attracted to each other too powerfully to be drawn asunder, or (ii) the molecules do not contain separate ions at all, but are groups of tightly-locked neutral atoms. It is probably the case that one and the same molecule can exhibit both of these states as different phases of its existence.

(*c*) Finally, the physical and the chemical characters of metals are interestingly correlated; for a piece of metal is now known to be not an assemblage of atoms merely, but an assemblage of positively-electrified atoms, the ions of that metal; and interwoven with these are the compensating units of negative electricity, the electrons, none of them fixedly attached to any special atom, but capable of being independent. The ions are positive because they are atoms, initially neutral, which have lost these negative electrons.

The lustre of a metal is the lustre of the electronic web; its power of allowing electricity so freely to pass is due to the freedom with which the dotted tracery of electrons can move through the interstices of the coarsely-grained ionic fabric, which itself remains immobile; it is these negative electrons which are shot forth when ultra-violet light falls on a metal and leaves it positively electrified; and, lastly, the chemical ability of a metal to dissolve in an acid and form a salt depends on the fact that the acid provides something positive (hydrogen ions) which can pair with these negative electrons and so leave the residual stack of metallic ions free to fall to pieces and pass as such into the liquid.

(*d*) *Gaseous Ions.*—The purely physical work initiated by Sir J. J. Thomson on the electrical conduction of gases has shown facts which have to do with the ions of solutions. It appears that from the molecules of elements in the gaseous form ions can be produced electrically, or by heat alone, which are the simple electrically-charged atoms, uncomplicated by any union with solvent-molecules. At present, the chief interest of these gaseous ions to us is, that the work which has to be expended in thus converting atoms to gaseous ions can be measured; and although the results are not yet all in order, nor by any means far advanced, it seems that the work or energy of electrically charging the various types of neutral atoms is being linked up with the chemical reactions which those same atoms undergo; for in such reactions the atoms use up or give out energy and are turned into ions and parts of chemical molecules. And, just as it is found by chemists that helium and its congeners are the most refractory of all elements to persuade into chemical activity, so it is found by the physicist that they of all gases have atoms the most difficult to ionise.

All this can be only touched upon and no more; it serves as one more reminder of the mutual supports which stretch across the structure of our science.

E. Conclusion

The real conclusion of this article is given at the beginning, and to that section the reader who has come thus far is asked to return. There is only this to add, and it will have leaped to the eye of any general chemist: this article has omitted reference to far more than it has included, and has passed by great fields of physico-chemical endeavour without so much as a hint. No word has been said of the study of chemical reactions in themselves, of the laws governing their speeds; nothing of the balance and play of the chemical competitions which have formed our earth's crust or have been produced in the laboratory, such as are summed up for the student in the phrases "chemical dynamics" and "phase-rule equilibria"; and, perhaps worst omission of all, almost nothing has been hinted of "chemical energetics," the study of the energy-evolutions which accompany and initiate chemical reactions. All these are of the essence of chemistry; without their study none of our basic industries is secure, nor can advance; yet they have been here relegated to the background, because they can be looked upon as subsidiary to the main quest for the units of physical science.

Chemical energetics affords already much more than an abstruse mode of classification; it is beginning to throw light on the quantum of radiant energy itself, and will increasingly do so; yet for still a little while chemistry will receive from the quantum theory more than it will give to it.

Inasmuch as the subject of chemical energetics has already been essential to our knowledge of the molecule, of the atom, and of the ion, the reader must recognise that it has in this survey been utilised as regards results but unjustly ignored as regards performance; and he should seek in its farther study the immediate material for the worker of the ensuing era of physical science, as that science is defined in the introductory section which sets the key of this chapter.

THE STRUCTURE OF THE ATOM

By E. N. da C. Andrade, D.Sc.

Introductory.—The problem of investigating the structure of the atom is one of peculiar interest to British men of science, since so many of the pioneers of the atomic theory itself have been our countrymen. Boyle and Hooke, who dominated the chemistry and physics of their day, made many interesting speculations as to the nature, and even the size, of atoms, but the atomic theory, as now understood, may be said to have been originated by John Dalton, when he erected his system of chemistry on the foundation of the Law of Multiple Proportions. The first direct demonstrations of the actual existence of atoms made in recent times were based on a close investigation of that ceaseless motion of microscopic particles suspended in a fluid which is named the Brownian movement, after the English botanist who first observed it in 1827. The periodic law, so essentially bound up in the atomic theories of to-day, was adumbrated by Newlands in his Law of Octaves. The first suggestion that all atoms might be built up of one common substance was made by Prout—although, in a very general sense, some might claim that Boyle anticipated him—when he suggested, in 1815, that the hydrogen atom might be a common constituent, as, indeed, we believe to-day that it is. Coming to modern times, we find that the early considerations of the atom as a structure of electrons are associated with the name of J. J. Thomson, while the general theory of atomic structure universally accepted at the present day is due to Ernest Rutherford.* The experiments of Moseley, of Aston, and of C. T. R. Wilson are fundamental for all modern work on the atom. And while Niels Bohr, whose remarkable theory has had so great an influence on scientific thought, is a Dane, England can claim that it was in her universities that he developed his fundamental hypotheses, and that his original papers were published in her tongue and in English journals. Numerous and remarkable as have been the contributions of foreign men of science to atomic studies, it may be claimed confidently that nowhere has the atomic field been cultivated more successfully than in Britain.

The modern view of the structure of the atom is essentially an electrical theory of matter. In this respect it forms the last step of a general movement which has been taking place ever since Faraday co-ordinated electric and magnetic forces, and demonstrated a connection between magnetism and light—the tendency to express all physical and chemical phenomena in terms of electricity and electromagnetic theory. The work of Clerk-Maxwell and of Hertz demonstrated the electromagnetic nature of all forms of radiant energy propagated with the velocity of light; it has been left for the electron theory, which is so recent a thing that its founders are still living and full of scientific ardour, to bring together physics and chemistry as the investigation, from various aspects, of the electrical structure of the atom. The electron, the small indivisible charge of negative electricity, producible from any kind of matter, but yet always exactly the same, dominates modern physical science. There is overwhelming proof that electrons are one of the constituents of which all atoms are built. Atoms are normally neutral, and must therefore contain positive electricity as well as the negative electrons. The problem of the structure of the atom is to decide the nature of this positive electricity, how it is distributed, and how the electrons are grouped in the atom; to solve this fully is to have the key to all the enigmatical phenomena of physics and chemistry, of which optical and *X*-ray spectra, crystallisation, cohesion, compressibility, magnetism, valency, and general chemical behaviour may be mentioned as examples. Further, the study of the structure of the atom brings us to consider new sources

* Whom we may, perhaps, on this occasion, call an Empire product, since he was born of Scottish descent in New Zealand, and was for many years Professor of Physics at Montreal.

of energy which, if they ever become available, will save us the trouble of scratching the surface of the earth for those *débris* of long-dead plants which we call coal and oil. It is remotely possible that in the future a knowledge of atomic anatomy will be as important for the engineer as for the chemist and physicist.

The Nuclear Atom.—Whatever divergencies may exist on minor matters, there is universal agreement to-day that the atom has a nuclear structure, as first convincingly argued by Rutherford in 1911. That is, the positive charge is concentrated in a small space, or nucleus, at the centre of the atom, the electrons, in number sufficient to make the atom neutral as a whole, being distributed round it at distances which are large compared to the nucleus. If the nuclear charge be called Ze, where Z is a whole number and e the magnitude of the charge of an electron, there must be, of course, Z electrons. An atom is an extraordinarily loose structure, which may be compared—if I may gain pardon for so homely a simile—to a swarm of gnats round a small lead shot. The size of the atom, as generally considered, means the space surrounding the centre of the atom which acts as an impenetrable sphere to any other atom striking it with such velocities as atoms or molecules have at the ordinary temperature in virtue of their heat energy : thus the distance of closest approach between the centres of two similar atoms endowed with such velocities is called the diameter of the atom. This is apparently of about the same size as the sphere containing the outermost of the atomic electrons when the atom is in its normal, or most stable, state. Compared to this size, the nucleus is only about as big as a small shot in a cathedral; in other words, our gnats, few though they be—for even the heaviest atom has but 92 of them—guard a space as big as a cathedral from the gnats which, around a second shot, form a second atom. Most of the atom is empty space, occupied by a field of force which endows it with impenetrability to comparatively slow corpuscles. However, a fast-moving corpuscle—an electron with a velocity of a thousand miles a second or more, or an α-particle, which is the nucleus of a helium atom, shot at spontaneously with great speed by certain radioactive substances—can pass freely through the atom on account of its large kinetic energy. It was by subjecting thin metal foils to the bombardment of α-particles from Radium-*C*, and noting the angles through which the particles were deflected, that Rutherford obtained the evidence which originally enabled him to conclude that practically the whole mass, as well as the positive charge, of the atom is concentrated in a very small space. Only by the assumption of such a concentration can the very large angle, through which, every now and then, a particle is deflected, be explained. In other words, when the positively charged α-particle smashes through the atom, but does not pass close to the nucleus, it is only very slightly deflected, owing to its large kinetic energy, but when, as must occasionally happen, it passes close to the heavy nucleus, which, on account of its positive charge, repels it, a large deflection takes place. The paths of the α-particles are detected by the scintillations which are caused by their arrival on a small phosphorescent screen, for a single swift particle causes one momentary microscopic spot of light. It may be noted that the individual scintillations caused by the α-particles shot out by radium were first observed by Crookes in 1903, and exhibited by him in a simple little apparatus which he called the *spinthariscope*. In the hands of Rutherford, the scintillation method of observation has become a very powerful weapon of investigation which has enabled him to observe the artificial disintegration of atoms.

Another device for following the paths of single α-particles, which leads to confirmation of the nuclear theory, is offered by the beautiful method of C. T. R. Wilson, of Cambridge. He makes use of the fact that the ions which the α-particle produces in its passage through a gas

act as centres of condensation for water vapour. By letting the particles pass through moist air, and effecting a sudden cooling by suitable expansion, he causes tiny drops of water to deposit on the ions which strew its path : all the microscopic drops together form a visible track which appears as a continuous white line when photographed. Fig. 1 is reproduced from a photograph taken by Mr. Blackett, making use of this method. It shows the paths of several α-particles in oxygen, photographed from two points of view so that foreshortening effects may be eliminated from measurements made. Towards the left of the bundle is seen a forked track, which is due to the α-particle in question having passed so close to an oxygen nucleus that it has been deflected through an angle of 76°, while the struck nucleus has itself, in its rapid motion, produced a track which appears as the shorter limb of the fork. We have an actual picture of the collision of nuclei, from which the mass of the oxygen nucleus can be deduced : it is found to be the mass of the oxygen atom. The nuclear theory has received many striking confirmations

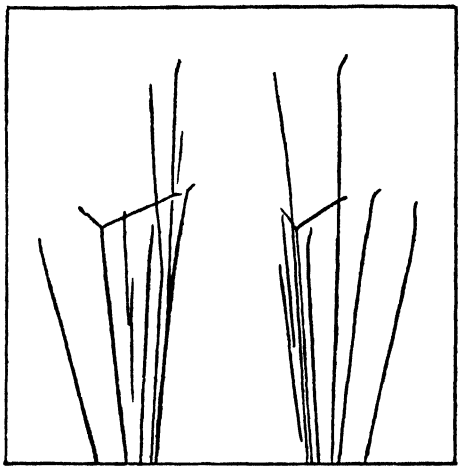


FIG. 1.

from experiments on these lines, and interesting investigations are now being carried out in the Cavendish laboratory by C. T. R. Wilson's method.

The Atomic Number.—The number which has been called Z, expressing the number of positive charges which characterise the electric action of the nucleus, has proved to be of the most fundamental importance, for it governs the general chemical and physical properties of the atom, if mass be excepted. If the elements be arranged in order of their atomic weight, and then numbered successively, so that hydrogen is 1, helium 2, lithium 3, sodium 11, and so on, the number attributed to each element is called the atomic number. It was one of the great services of H. G. J. Moseley, the brilliant young English physicist who was killed in Gallipoli at the age of twenty-eight, to establish clearly that this atomic number is, in general, of deeper significance for atomic behaviour than the atomic weight. It is only ten years since he did this, yet already the time when the atomic weight was the only thing taken into account seems very remote. Moseley drew his conclusions as a result of his pioneer measurement of the wave-lengths of the so-called characteristic X-rays obtained from the various elements, which he measured by means of the method of crystal reflexion developed by W. H. and W. L. Bragg. He found that the

square root of the vibration frequency of one line of a given X-ray series (say the α-line of the K-series) gave a smooth curve, approximately a straight line, when plotted against the atomic number, but an irregular "lumpy" curve when plotted against atomic weight. Fig. 2 shows this clearly. He concluded that the atomic number must be the same as the number Z denoting

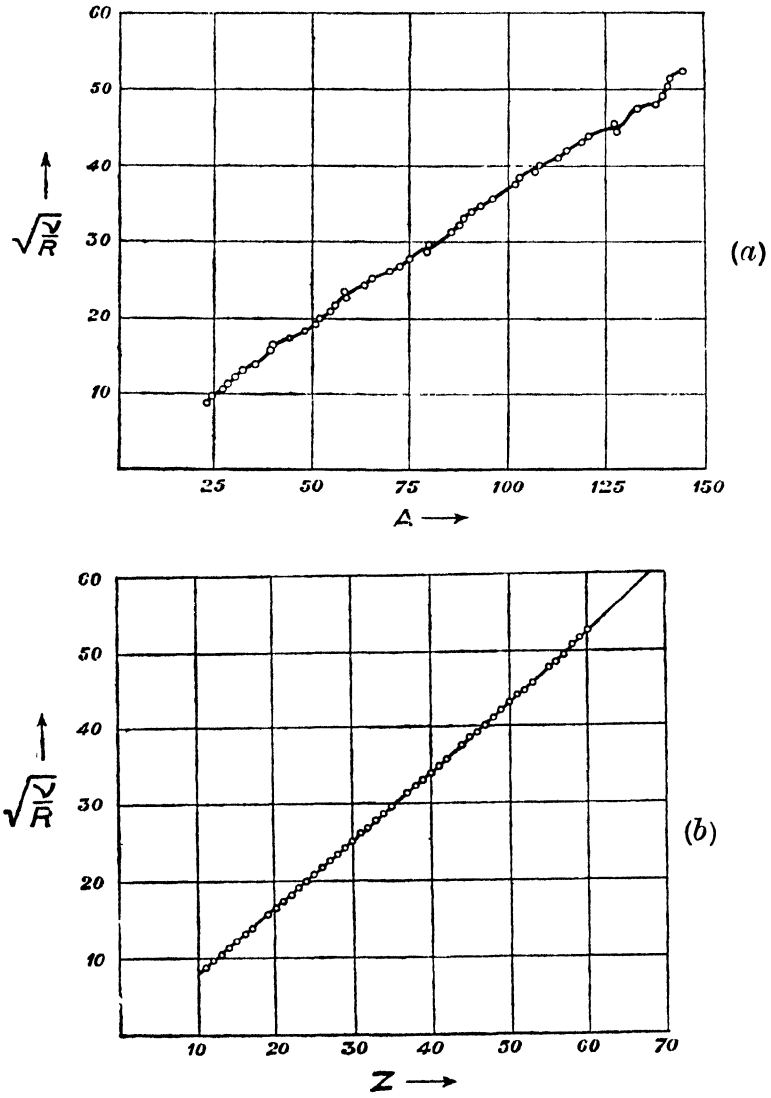


FIG. 2.

the net positive charge on the nucleus, or, in his own words, we have in the regularity of curve (*b*) of Fig. 2 "a proof that there is in the atom a fundamental quantity which increases by regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus." This essential feature of all modern atomic theory has been verified

directly by Rutherford and his school, by the help of experiments on the scattering of α-particles by matter, to which reference has already been made. The recognition of the importance of the atomic number has introduced some notable simplifications into chemical theory. Before Moseley's work there had always been trouble about the position of argon and potassium, and of cobalt and nickel in the periodic table when the elements were arranged in order of the atomic weight. If the atomic numbers of potassium, cobalt, and nickel be determined by measurement of the frequency of the characteristic X-rays, the order turns out to be that to be anticipated from the chemical properties. The atomic weights have a comparatively superficial relation to the chemistry of the elements. It will be seen, therefore, that the definition of the atomic number as the ordinal number of the elements when they are arranged in order of ascending atomic weights must be corrected by the X-ray measurements, which really serve to determine the number. The X-ray frequencies also offer the clearest indication of the gaps which remain to be filled by the discovery of new elements, since it is only a question of detecting a missing whole number from a curve of type (*b*), Fig. 2. A large number of most accurate measurements of X-ray spectra have been made by Moseley's followers in Sweden, Germany, France, and England, and we are now confident that only five elements, having atomic numbers 43, 61, 75, 85, and 87, remain to be discovered, one of the six missing in Moseley's time having been supplied by the recent isolation of hafnium. All the results mentioned are, of course, dependent on the fact that the characteristic spectra of the elements, being conditioned by the interior structure of the atom, are atomic properties, that is, independent of the state of chemical combination of the atoms in question.

Isotopes.—The nuclear charge, then, is in its nature some simple multiple of the charge on the electron, but, of course, positive. The atomic weight, however, whether it be expressed in terms of that of hydrogen or that of oxygen, is not in general a whole number, and it is this fact which has always stood in the way of the acceptance of Prout's hypothesis. The work of the last few years has furnished an elegant explanation of the existence of fractional atomic weights, and has introduced great simplicity into what was before inextricable complication, namely, the relations of the atomic weights to one another. The essence of the theory of isotopes, which has been almost entirely developed in England, is that atoms of different mass can have the same chemical properties, whereas until recently it was always assumed by the orthodox that given chemical properties were inevitably connected with one perfectly definite kind of atom alone. By the orthodox, because as long ago as 1887 Crookes foreshadowed the theory when he suggested that the atomic weights might be mean values for atoms of a large number of different weights.

Isotopes were first experimentally detected among the radioactive elements, when it was found that certain of them, such as thorium and ionium, which differ widely in radioactive properties, were chemically inseparable, and should occupy the same place in the periodic table.* The method, however, which has demonstrated the far-reaching application of the isotopic principle, and made of it an actual method of correcting atomic weights, is the method of positive ray investigation initiated by J. J. Thomson, and brought to great perfection by F. W. Aston, also working at Cambridge. These positive rays, or, as I have suggested calling them, mass rays (since the essential thing about them is that they consist of a stream of atoms or molecules, which need not always be positively charged) can be obtained in various ways. J. J. Thomson and Aston have in general used a pierced cathode of particular form, through the channel in which

* Whence the name, suggested by F. Soddy—*isos*, the same, and *topos*, place.

the mass rays are projected when a discharge is passed through the exhausted tube containing traces of the gas to be investigated, but a heated anode containing a paste made up of a salt of the element in question has also been employed to originate the rays, especially by Dempster. The ratio of the charge to the mass of the particles which constitute the pencil of mass rays can be obtained by subjecting the beam to the joint action of an electric and a magnetic field, and recording the resulting deflection on a photographic plate placed at right angles to the original direction of the beam. Aston's successes have been rendered possible by his adoption of a particular arrangement of the electric and magnetic fields, as a result of which the deflected beam may be focussed sharply on a single spot, instead of being spread into a comparatively broad parabolic strip as it was in the original method. This allows shorter exposure combined with greater accuracy. The ratio of the charge to the mass being known the mass can usually be determined with but little trouble, since the charge is in general either one or two units, and simple checks discriminate between the cases of single and multiple charges. Aston can now measure the atomic weight by the method of mass rays with an accuracy of 1 part in 1000 parts, and has been able to show, for instance, that the atomic weight generally accepted for antimony was too low. When the element being investigated is present as a gas, less than one-tenth of a milligram is used for an atomic weight determination; when an anode paste is used, somewhat more is, of course, required. Mainly as a result of his labours it has now been proved in the case of all elements so far investigated (that is, about half the total number of the elements) that while those of which the atomic weights, expressed in terms of oxygen as 16, are whole numbers consist of one kind of atom only, on the other hand, those of which the atomic weights contain a fraction do so because they are mixtures of atoms of identical chemical properties, but different masses, these masses being themselves whole numbers. Thus chlorine, of atomic weight 35·46, consists of atoms of mass 35 and 37; zinc, of atomic weight 65·37, contains four isotopes of masses 64, 66, 68, 70; while tin contains as many as seven isotopes. It should be added that, although the isotopes are by their nature *chemically* inseparable, they may be at any rate partially separated by making use of certain physical properties governed by mass alone, such as the rate of diffusion, or, speaking more generally, the gas-kinetic velocity. By ingenious methods based on the principle indicated, the two isotopes of neon have been partially separated, as proved by density measurements: the two chlorines have been partially separated, in the form of HCl; while from ordinary liquid mercury mercuries have been obtained possessing densities of 0·99974 and 1·00023 respectively, if the density of the original substance be taken as unity.

Aston's work has proved, then, that in all the large number of cases examined the atomic weights of individual atoms are simple multiples of one-sixteenth of the weight of the oxygen atom, oxygen, luckily, having no isotope. This is often alluded to as the whole number rule. The objection to Prout's hypothesis is no longer valid, and we can assume that in all atoms the mass is contributed by a common constituent. This common constituent is the hydrogen nucleus, or *proton*, that is, a hydrogen atom which has lost its one electron. It is believed, then, that all atoms are built up ultimately of two constituents, the proton and the electron, the mass of the electrons being negligible compared to that of the protons.

The existence of isotopes is simply explained by the modern view of the nucleus. The mass of the nucleus is due to the protons in it, each of which must contribute one unit of mass and one unit of positive charge. The nucleus must also contain electrons—not to be confused with the extranuclear electrons already discussed—for otherwise, for all atoms, the atomic number would equal the atomic mass, which is actually the case for hydrogen alone. Exactly how these

electrons and protons are held together in the nucleus is not known, but they must be there. Now if a positive proton and a negative electron be successively removed from a nucleus the charge of the nucleus as a whole, which conditions the chemical properties, is unaffected, but the mass is diminished. An isotope is formed. This theory is much strengthened by the consideration of radioactive substances. An α-particle has mass 4 and 2 positive charges : everything tends to show that it is a particularly stable combination of 4 protons and 2 electrons. Now when a radioactive nucleus has lost, in successive ray changes, one α-particle and two electrons, as happens in each of the radioactive series, a product which has the same nuclear charge, and consequently chemical properties, as the parent substance, but a mass less by 4, is to be anticipated. This anticipation is in exact agreement with what is found experimentally.

Atomic Energy and its Availability

An objection to the theory that the mass of all nuclei is due to protons immediately occurs, namely, that the atomic weight of hydrogen is not 1, but 1·0077, in terms of oxygen as 16. This has been met by arguments which lead to speculations of the first importance. The hypothesis to be justified is that packing the protons close together to form heavier nuclei the size of which is but little larger than their own leads to a slight loss of mass. The electromagnetic theory of mass does, in fact, indicate such loss, since the inertia of an electric charge depends upon the space in which it is concentrated, but the problem arises as to what has become of the mass. On all older theories mass is indestructible, but according to Einstein's theory of the equivalence of mass and energy a loss of mass can be compensated by a release of an amount of energy which calculation shows to be very large. In fact, it follows from the theory that if four protons, which when separated have a total mass 4·0308, should combine to form a helium nucleus, 5×10^{-5} ergs of energy would be set free. This may not sound very much, but it is equivalent to saying that if a gram-molecule of helium could be made out of the necessary hydrogen atoms 7×10^{11} calories would be set loose, or some hundred million times as much heat as is produced by the burning of an equal weight of coal. To put the matter in an engineering form, one ounce of helium in the course of formation from hydrogen should yield a million horse power for seven hours. This exceeds the transformations dreamt of by the alchemists, but so far we cannot see our way to making hydrogen nuclei stick together with the cement of two electrons. Perhaps we shall one day get, with great difficulty, a few atoms of helium so to form, which will satisfy the man of science; perhaps we shall get a controlled rate of formation in appreciable quantities, which will satisfy the engineer; perhaps we shall get an uncontrolled and cumulative rate of formation which will destroy the experimenter, and satisfy certain religious sects who object to experiments as impious : or will destroy the world and satisfy nobody. This is mere speculation, but one can scarcely refrain from speculation at the thought of these enormous supplies of energy associated with so small a weight of matter. In any case nuclear chemistry, which is at its very beginning, is bound to furnish sensational results.

This chemistry of the nucleus has been begun by Rutherford, who in an extraordinary series of experiments has succeeded in obtaining definite proof that he has disrupted certain nuclei. He bombards nitrogen with a stream of α-particles, and is able to show by the scintillation method that long-range protons are produced : elaborate controls demonstrate that the only possible source of these protons is the nitrogen nucleus. Since the original experiments of 1919 Rutherford and his collaborators, of whom Chadwick deserves special mention, have shown that such

protons can be struck out from the nuclei of a variety of light elements. It is particularly noteworthy that in the case of aluminium the proton produced has a greater energy than the striking α-particle. In other words, some of the energy of the nucleus has been transformed into kinetic energy of the proton, or, in a sense, a fraction of the nuclear energy has been liberated, although in no way made available. Lest it should be hastily assumed that practical developments are to be anticipated in the near future, it may be pointed out that the whole α-radiation from a gram of radium, costing some thousands of pounds sterling, will in favourable circumstances release a few calories from aluminium, an amount of heat, that is, which can be produced by the burning of a few grains of coal dust. The theoretical importance of the results, however, is immense. They confirm the hypothesis that protons enter into the structure of the nucleus, and show that, on this small scale, it is possible to transform heavier elements into lighter ones, but not, so far, lighter into heavier elements. For nitrogen which has lost a proton becomes carbon; aluminium which has lost a proton becomes magnesium; and so on.

This atomic chemistry (which has been developed by physicists) is a thing of the last fifteen years—in fact most of the chief advances have been made since the War. The essential information has been won by dealing with single atoms, or very few atoms, and following their electrical and dynamical behaviour by means of a new technique which has been worked out by J. J. Thomson, E. Rutherford, C. T. R. Wilson, F. W. Aston and their followers. The older chemists dealt always with thousands of millions of atoms at a time, and gave us certain average results in which things which we are only now beginning to disentangle were confounded.

The Extranuclear Electrons and Their Arrangement

We now direct attention to those electrons which are sparsely grouped about the nucleus and form what may be called the extra-nuclear structure. The behaviour and location of these have been elucidated mainly by three lines of study—*X*-ray spectra, optical spectra, and chemical combination.

The whole subject of spectra, both optical and *X*-ray, has been revolutionised in the last eleven years by the theory of the Danish physicist Bohr, who was working in Manchester under Rutherford when he published his epoch-making papers on "The Constitution of Atoms and Molecules." His theory breaks away from classical electrodynamics, according to which an electron moving in a closed orbit should emit a radiation the frequency of which is that of the revolution of the electron, and invokes the quantum theory, applied in a particular way, to determine the frequency of the radiation emitted by an atom. This is not the place for any attempt at an exposition of the theory, but it may be recalled that he postulates certain "stationary" states, in which the electron circulates in selected orbits without radiating at all. If, however, the electron passes discontinuously from one "stationary" orbit to another the consequent change of energy E is accompanied by a radiation the frequency of which is given by the fundamental quantum relation $E = h\nu$, where ν is the frequency and h is a constant. The angular momentum in possible orbits is governed by certain dynamical relations, which also involve the quantum theory. Not only have the line spectra of hydrogen and of ionised helium been worked out in the greatest detail, but the fine structure of their spectral lines has been connected up in one comprehensive formula with the so-called *X*-ray doublets. Further, a general theory of spectra has been evolved, in deriving which Bohr makes great use of a principle which shows that there is a certain correspondence between the classical theory and the quantum

theory of radiation—the celebrated correspondence principle, which forms a bridge between the new and the old point of view. Bohr's methods have enabled him to deduce, largely from the spectra, a general theory of atomic structure which explains many features of the periodic system much better than any previous theory, and has already led to the discovery of the element hafnium, of atomic number 72. Before discussing, very briefly, Bohr's views, a word is needed as to the relation between optical and X-ray spectra.

The spectra of characteristic X-rays are atomic in nature, that is, a given element gives a determined line spectrum, which is (apart from a minute effect) independent of the state of chemical combination in which the element may be. The interpretation of this is that the X-ray spectra are due to the more closely bound electrons of an atom, which play no part in chemical combination, that being an affair of the exterior, or, more correctly, the loosely-bound electrons. The regular progression of the frequency of a given X-ray line as we go from one atom to the next, which makes little account of the end of one period and the beginning of the next, shows that, as a first approximation, the inner structure of a given atom is a part of the inner structure of all heavier atoms. The optical spectra, however, are due to transitions between electronic orbits which lie near the periphery of, or quite external to, the atom. These orbits are involved in changes of chemical character, so that the optical spectra show abrupt changes in nature as we pass from element to element, especially at the end of periods, and are also profoundly modified by the state of chemical combination of the atom. Bohr, in his theory, makes use of both optical and X-ray spectra.

According to him, the orbits of electrons in the atom fall into classes, each class being characterised by a certain *total quantum number*. Each class contains different states—circular orbits, and elliptical orbits of a few determined eccentricities, the eccentricity being governed by an auxiliary quantum number, usually written as a suffix to the total quantum number, thus : 3_2. Successive periods in the periodic arrangement are characterised by the highest total quantum number represented in the atom. Thus with hydrogen and helium the total quantum number is 1, and the orbits of the two electrons of neutral helium are both circular and equal, their planes being inclined to one another. In the period lithium–neon the two inner electrons have orbits similar to those of helium, while the others have orbits of total quantum number 2, both circular and elliptical being present in the heavier elements. The period sodium–argon has, in addition, 3 quantum orbits : the next period acquires 4 quantum orbits ; and so on. The great importance of the theory for the chemist is that it indicates, much better than any other, the true nature of the long periods. It shows that there are never, even in the heavier elements of a long period, more than 8 electrons of the highest quantum number—outer electrons, they may be called, although in tracing out their elliptical orbits they have to pass through the interior of the atom. In the long periods, after the first one or two electrons have been added in orbits of highest quantum number, the next electrons go to complete a group of lower quantum number, which the addition of the first electrons has made, in a certain way, incomplete. Of the 18 electrons added, for instance, in the period potassium–krypton only 8 have total quantum number 4 : the others go to add to the orbits of total quantum number 3, which the formation of a higher group has made capable of receiving new numbers. Speaking in a very general way, the electrons added in long periods go, when a certain stage is reached, to add to the inner structure of the atom, instead of accumulating outside. This forms a great contrast with Langmuir's theory, in which a completed period forms a part of all heavier atoms. Bohr's theory has been strongly confirmed by certain inconspicuous periodicities in the X-ray spectra which were passed over in the earlier

work, but have now been revealed. It achieved a brilliant triumph when it predicted that the then unknown element of atomic number 72 should resemble zirconium and thorium, and not the trivalent rare earths. This prediction led to the work of Hevesy and Coster, who discovered the new element hafnium (named from Hafnia, the old name for Copenhagen) which markedly resembles zirconium, and is not a rare earth. It is found in zirconium minerals, the conjunction of homologous elements in nature being well known to chemists, and an X-ray method of

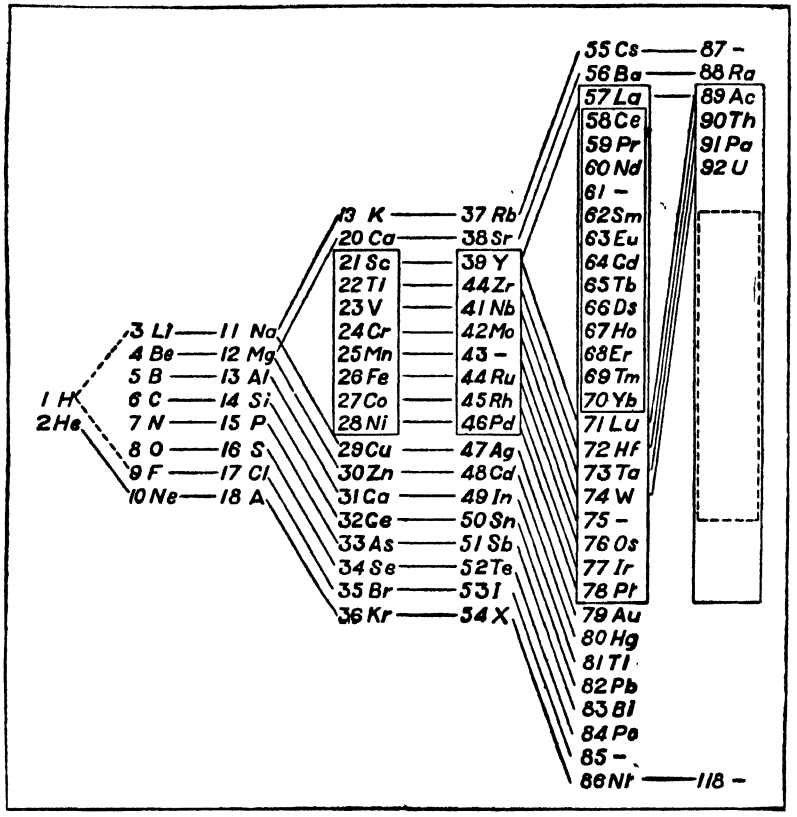


Fig. 3.

rapidly estimating the proportion of hafnium in a zirconium ore has been worked out. The new element is by no means rare, it being estimated to form 0·001% of the earth's crust.

Bohr's scheme is indicated in the table of Fig. 3, where the elements in which there is an internal rearrangement or reconstruction of the inner parts are enclosed in frames. Fig. 4 shows in a rough way the structure of a few of the simpler atoms according to Bohr's ideas. The elliptical orbits,* which are shown closed for simplicity, should really be slightly open, as they do not exactly repeat themselves, but form rosettes. The apparently elliptical orbits just enclosed in a circle † are really circular orbits the planes of which are inclined to the plane of the paper.

* Marked 2_1 in the case of neon.

† Marked 2_2 in the case of neon.

Valency and Atomic Structure

While there is little doubt that the electrons must really be moving in orbits somewhat in the way described in Bohr's theory, it is not easy to use such a dynamic atom for considerations of chemical combination, since it is hard to see how the moving electrons of one atom interact on those of another atom. G. N. Lewis has shown how, by considering the outer electrons to be

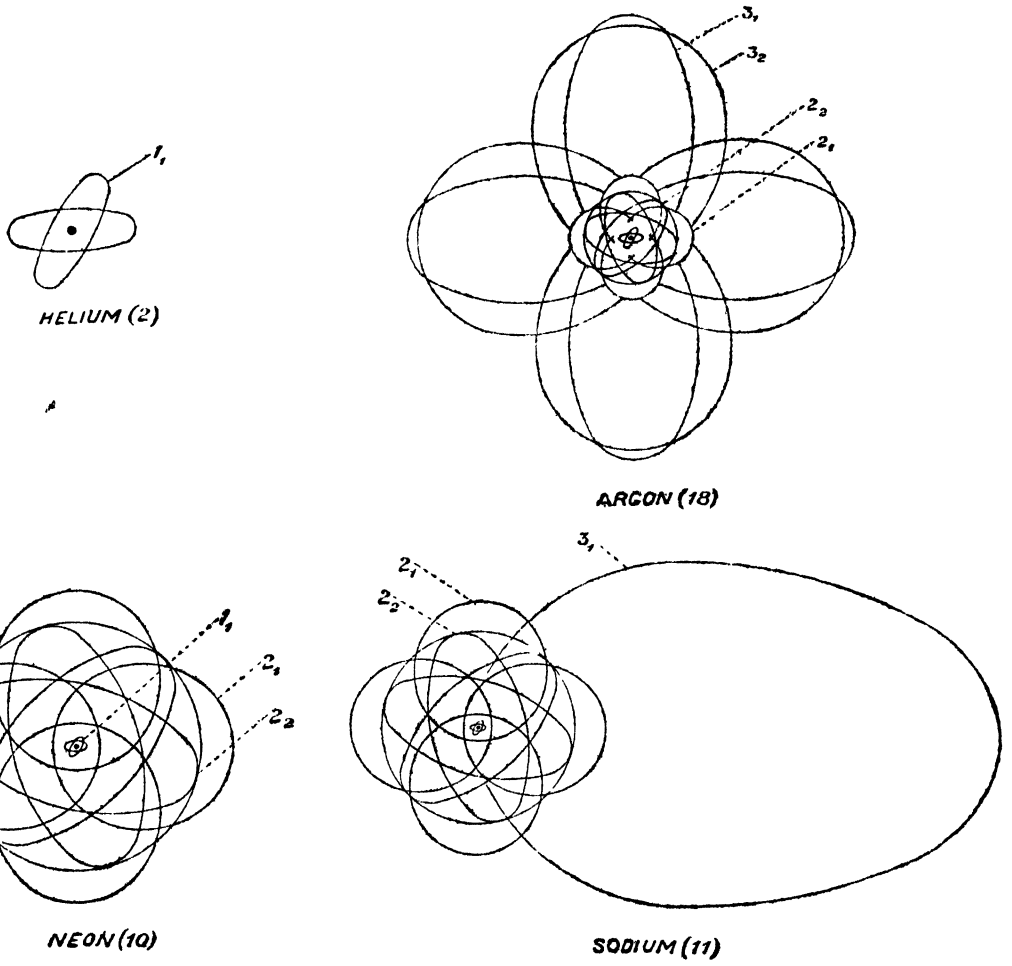


Fig. 4.

stationary, a variety of facts of chemical combination can be strikingly described, and he has been followed by Langmuir, who has added certain hypotheses, and adduced chemical and physical data in support of them. Lewis's theory of the atom may be, in a sense, incorrect, but it is of great value, in offering a simple pictorial representation of many hitherto disconnected phenomena. To take an analogy from a familiar branch of chemistry, the carbon atoms in a benzene

molecule are certainly not really arranged in a plane hexagon, but it is often very convenient to consider them so.

According to the school of Lewis, which has found much support in the work of Kossel, the outer electrons, which never exceed eight in number, are responsible for chemical combination. In the case of the rare gases the outer layer is complete, and the eight lie at the corners of a cube. If in an atom there are less than the eight in the outer layer, that atom can take up electrons until the layer of eight is completed : it can also give up any or all electrons of the layer. This expresses Abegg's rule that the sum of maximum positive and negative valencies for a given element is 8. A preliminary to the formation of polar compounds is the ionisation of the atoms

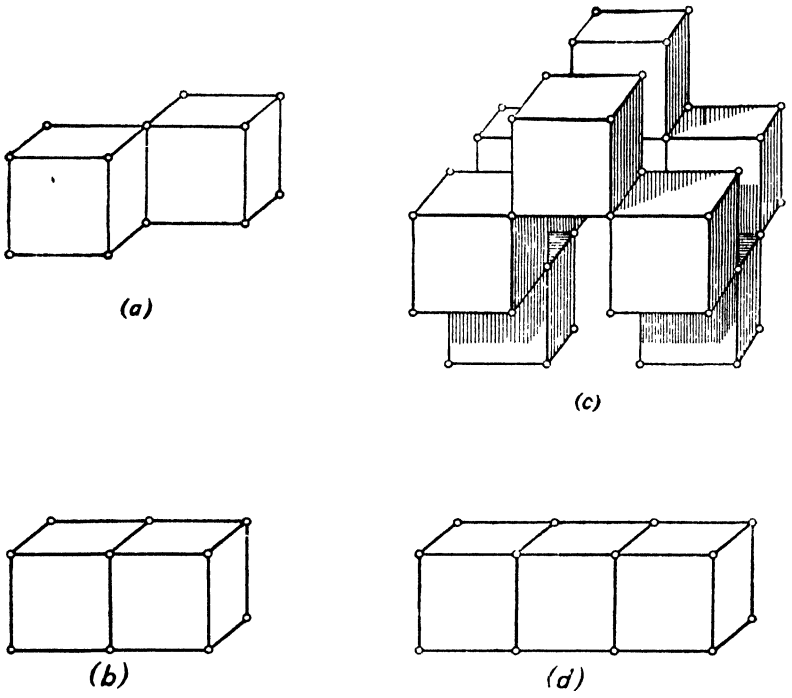


FIG. 5.

by interchange of electrons between outer layers. An essential novelty of Lewis's presentation is that he assumes it possible for atoms to hold pairs of electrons (or duplets, as they are called), but not single electrons, in common, which aids considerably in picturing homœopolar compounds. The expression *co-valency* has been introduced to denote this sharing of electrons, the degree of covalence being measured by the number of pairs shared. There is no space here for examples of the application of the ingenious octet theory of valency—suffice to say that it has been eagerly taken up, in England as elsewhere, and successfully applied to a variety of problems. Fig. 5 shows some models of molecules on the cube theory.

The modern electrical theory of combination is distinguished from the old electrical theory, which met with so many obstacles, especially as regards homœopolar compounds, in considering the atom as a structure of positive and negative electricity, and not as a positively or negatively

charged whole. An atom which is neutral, say a neutral nitrogen atom, can still exert an electrical force locally, since it has in the nucleus and its surrounding electrons a positively charged kernel the attraction of which is not everywhere neutralised by the five outer electrons. It can hold, besides these, charged atoms, if they are presented ready charged. Thus nitrogen can hold an HCl molecule, for the Cl in the HCl has taken an electron from the H to complete its own outer layer to 8 : the H is thus negatively charged, and is attracted by the N kernel. A whole theory of complex salts has been worked out on these lines.

The Bohr and the Lewis view of the outer structure of the atom are not in essence irreconcilable, in spite of the great apparent difference that in the former the electrons are moving in large orbits, and in the latter are at rest at the corners of an imaginary cube. Lewis contends that the atom behaves chemically *as if* the outer electrons are fixed and attain a particularly stable arrangement when eight in number. In Bohr's theory the outer structure is completed by eight orbits. An electron orbit is probably a closer representation of atomic structure than a fixed electron, but apparently it may be replaced by a stationary electron for the purpose of considering chemical combination. Thus, referring to Fig. 4, the large loop evidently represents an electron which will behave quite differently as regards its action on other atoms from all the other electrons in the sodium atom, and, until we know more clearly how it can influence the outer orbits of other atoms we can, it seems, gain some clearness by postulating in its stead a fixed electron at one corner of an outer cube, for the behaviour of which certain rules have been deduced from chemical experience.

Conclusion.—In conclusion, we may ask ourselves what has been really achieved by all the investigations which during the past thirteen years have been devoted to the problem of the Structure of the Atom, investigations in which, in spite of the War, our own land has played so prominent a part. Choosing a few of the chief results, it may be replied that the whole question of the structure of matter has been simplified by a reduction of the ultimate components to two, the proton and the electron : that the relations of matter and radiant energy to one another have been placed on a new foundation : that the whole question of fractional atomic weights has been cleared up, the problems of valency have been simplified, the chemistry of the radioactive elements has been brought into closer touch with that of the other elements : that the structure of optical and X-ray spectra has been proved subject to certain general rules, and brought into touch with the problem of the periodic structure of the elements, with the discovery of a new element as one result; while an attack on the recondite problems of magnetism has been successfully initiated. That these headings, comprehensive as they are, can be criticised as leaving out important aspects of recent advances is certain, for the scope of the new discoveries and speculations is too wide to be indicated in a few phrases. New types of investigation have arisen in which single atoms are handled, a new class of theories holds the field, in which classical mechanics and electrodynamics are set aside in favour of daring hypotheses, the boldness of which is justified by their success. Further work is leading to a reconciliation of the old and the new : the future may be confidently expected to show us the wider significance of many laws which are at present little more than mysterious rules producing right results. The study of the Structure of the Atom is young and full of difficulties, but there can be little doubt that the harvest so far gathered has abundantly justified all the labour spent in cultivating the atomic field.

CRYSTALLOGRAPHY

By T. V. Barker, M.A.

Foreword by Sir Henry Miers, F.R.S.

Since early times crystals have attracted attention and excited interest by reason of the beauty and symmetry of their form: the best examples were to be found in the mineral kingdom and provoked study on the part of mineralogists, so that till recently crystallography was almost regarded as a branch of mineralogy. In reality, the crystals of substances prepared in the laboratory of the chemist are of even greater scientific interest than minerals.

The crystal form is the one naturally assumed by a substance when it becomes solid; it expresses an inherent property of the material of which the crystal consists.

The form of the crystal—whether salt, sugar, alum, borax, ice, or any other substance—is obviously due to the manner in which the atoms or molecules or particles of the crystallising material marshal themselves; and this must depend upon the attractions and repulsions or linkages between them, whether owing to the action of the electrons or other cause.

The study of these remarkable forms, and of the structures of which they are the expression, has for more than a hundred years been eagerly pursued as likely to throw light upon the nature of the atoms or molecules and their groupings.

The last century saw the geometrical study of a vast number of crystals completely worked out: their form and symmetry were accurately determined; the causes of their resemblances and differences were established, and the manner of their harmonious mixing was traced. The century also saw every available physical method brought to bear upon the investigation of their ultra-microscopic structure.

By the close of the century it had been proved that the symmetry of crystals is quite peculiar, in that their faces are repeated in a 2-, 3-, 4-, or 6-fold manner, but never in a 5-fold manner, so that they differ completely in this respect from the living organism, in which 5-fold repetition (*e.g.* of petals) is common; it had also been proved that this absence of 5-fold, and of anything greater than 6-fold symmetry, is simply due to the fact that they are perfectly homogeneous: in this respect also they differ from living organisms. It had further been fully established that if classified by the symmetry of their structure they must belong to one of 230 possible types.

Chief among the physical tests employed in this study was the optical probe; the passage of light through transparent crystals is attended by such remarkable features that the polarisation and refraction of light in this process became the most potent and practical instrument by which crystals could be determined and identified. This method of investigation revolutionised the study of rocks and meteorites.

The enquiry was, moreover, reversed: the optical properties of crystals were directed to the study of the reflected and refracted beams, and contributed most valuable information concerning the nature of light.

In the present century this history has been repeated, but with other methods and with even more startling consequences. The far smaller undulations characteristic of *X*-rays have been turned upon crystals and employed to reveal the intricacies of their structure, just as light waves had been employed previously. The crystals, in return, have helped physicists to understand the nature of *X*-rays.

With the old optical and geometrical methods the *relative* arrangements of the material in

a crystal structure along different directions could be determined, but not the actual distances that separate the particles of which the crystal consists; neither was it possible to say what positions are occupied by the atoms themselves in the structure. The *X*-ray methods of investigation seem able to answer both these questions. They constitute a very remarkable advance, and are fraught with great possibilities.

From the foregoing it will be understood that, from the point of view of pure science, crystals are most fruitful subjects of study. From the practical point of view, they have also no small importance.

The process of crystallisation rejects impurities and is used by the chemist, the sugar refiner, the salt manufacturer, etc., to produce pure material; the ruby and other gem stones can be reproduced by the same process; many other crystallised minerals have valuable properties; for example, the thin sheets of mica used for various purposes can only be obtained from large natural crystals; the apparatus used for submarine signalling, and the receivers in wireless telegraphy (" crystal sets ") depend upon subtle electric properties of crystals for their application to modern needs. Metals and alloys consist of crystals the properties of which determine those of the mass; the movements of glaciers probably depend to some extent upon the peculiar slipping of the ice crystals of which they are composed.

Again, a substance may often be identified from a minute crystal under the microscope without the sacrifice of any portion of it such as is involved by chemical analysis : in mineralogy and geology this is of vital importance; and in the same way the pathologist and botanist are enabled to determine the nature of the minute crystalline deposits in animal and vegetable tissues.

To the theoretical and practical study of crystallography the contributions of British investigators have been of the highest importance, ranging from the invention by Wollaston of the reflecting goniometer, to the more recent discoveries of the present century.

H. A. M.

The Nature of a Crystal

The salient feature of a crystal, that of definite form, did not pass unnoticed by the Ancients. Quartz, for example, was stated to be hexagonal, and this unquestionable geometrical affinity with ice (" Krystallos ") may have fostered a belief in their identity—a foregone conclusion, in any case, in a world constructed of qualities. Now it is a long story, indeed, from the earth, air, fire, and water of Aristotle to the 92 elements of Moseley, but it is inseparably connected with crystals. For what is a crystal but a peculiar quality of matter ? And was it not a crystal that inscribed the record at the first roll-call of elementary substances ? Any writer on crystals has therefore an ideal theme, and must look to himself if the result be devoid of interest.

It is to later mediæval times that one must turn for any definitely expanding knowledge of crystals. Both the search of the miner for useful metals and the pitiful attempts at a replacement of gold by pinchbeck led to a gradual recognition, not only by weight and colour, but also by shape of ores and fluxes, as also of the " heavy chemicals " obtainable therefrom by the help of acids. And a later recapture of the Greek spirit of enquiry for its own sake finally led Steno (1669) and others to the proof that crystals are subject to an exact rule of Nature.

Steno showed that, however much the quartz crystal of Fig. 1 may deviate from the ideal symmetry of Fig. 2, there is really no element of chaos. For the slope of the six pyramidal faces, p, is constant, and the external inclination of the prisms, m, always one of 60°. So that one figure is derivable from the other by a gentle planing away of the smaller prism face, m_2, or by a converse deposition of material on all the others in any subsequent process of growth. But no such simple expedient will serve to transform the one or the other into the shape assumed by alum (Fig. 3). Crystalline form, then, appeared to be a specific property conferred on each substance by the operation of a mysterious force or quality.

Such patient angular determinations culminated in the comprehensive work of de Romé Delisle (*ob.* 1790), who measured and described everything within his reach. But collections of facts are mere aggregations. Something more is needed if they are to become a Science—a quickening by the Spirit that never fails to transmute dead matter into an Organic Growth. The grand induction in this province was made by the Abbé Haüy, whose generalisation embraced the crystals of his day and also the thousands of ours, and will no doubt be applicable to the multitudes of the future.

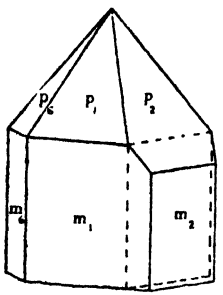


FIG. 1.—DISTORTED CRYSTAL OF QUARTZ.

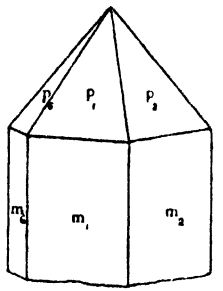


FIG. 2.—IDEAL CRYSTAL OF QUARTZ.

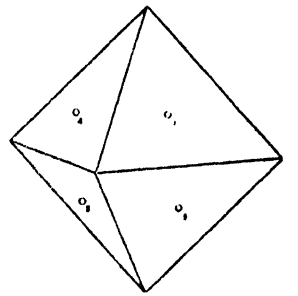


FIG. 3.—OCTAHEDRON OF ALUM.

Haüy commenced his work by breaking crystals along their natural planes of cleavage. He was not the first "crystalloclast," as Delisle would have us believe, being in fact preceded by many others. There was, for example, Westfeld and then the mineralogist Gahn (an odd corruption of an ancestral surname Geddes). Both had split up Iceland spar into rhomboidal particles, and the latter had reconstructed them into a model of "Dog-Tooth spar," another variety of calcite. Independently going over the same ground, Haüy went forward to results which we can best outline in the later language of Bravais (1848).

Crystals of common salt naturally take the form of a cube, modified at the eight corners by facets of variable size but constant inclination (Fig. 4). They can be readily cleaved into flakes parallel to any cube face, but not in any other direction; so that a large crystal is reducible to a mass of cubes, the smallness of which is only limited by the coarseness of the blade at our disposal. Atomistically, however, there must be an end to the process of sub-division—an end more rapidly obtained by dissolving the crystal in a liquid menstruum. Conversely, there must be a beginning, and the crystal originates when eight ultimate particles come together out of the solution and arrange themselves at the corners of a cube (Fig. 5). If conditions are favourable (the solution supersaturated), this fundamental cell will serve as a rallying point and

the crystal grows retaining its cubic outline as in Fig. 6; but if particles are attracted more slowly to the corners than to the middle of the sides, facets (Fig. 7) must make their appearance at the corners. The essence of a crystal, then, does not lie so much on the surface as in the interior. In sharp contrast with an ordinary liquid or vapour, the internal arrangement is of the utmost regularity, every particle playing the same *rôle* and being similarly surrounded

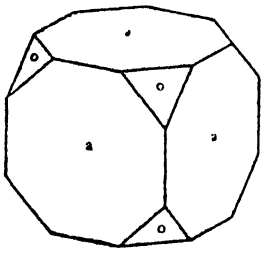


FIG. 4.—CUBE OF COMMON SALT WITH OCTAHEDRAL FACETS.

FIG. 5.—STRUCTURAL CELL OF COMMON SALT.

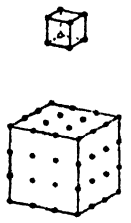


FIG. 6.—CUBE OF COMMON SALT SHOWING STRUCTURAL DETAILS.

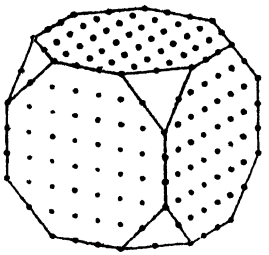


FIG. 7.—CUBO-OCTAHEDRON SHOWING STRUCTURAL DETAILS.

by the remainder. The particles are strung out at equal intervals along any selected line, and the same is true of successive plane strata. Further, an actual inspection of a model would reveal certain sets of internal planes which stand out from all others, the particles in them being aggregated more closely together. Such densely packed planes are the natural boundary surfaces of a growing crystal, and at the same time possible directions of cleavage; and by

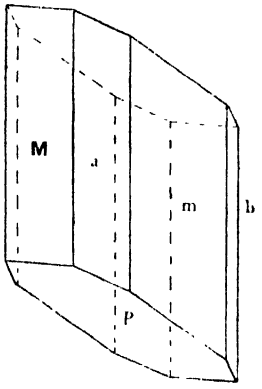


FIG. 8.—SIMPLE CRYSTAL OF COPPER SULPHATE.



FIG. 9.—STRUCTURAL CELL OF COPPER SULPHATE.

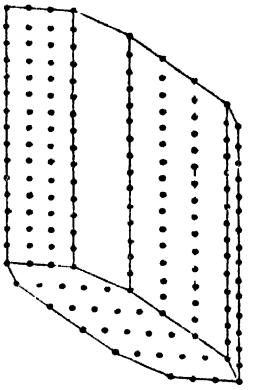


FIG. 10.—COPPER SULPHATE CRYSTAL WITH STRUCTURAL DETAILS.

studying the internal details of a model of the structure it could be predicted which new facets are likely to be developed, if the conditions of crystallisation (temperature or pressure or solvent) be altered.

Armed with such ideas, Haüy made a triumphal progress through the mineral kingdom, determining the shape of the fundamental cell by trials of cleavage, and checking its relative dimensions (where they are not equal as in a cube) by simple geometrical considerations based

on measured angles. Judged by modern standards, his goniometer was but a poor instrument, but his enthusiasm and his rare insight carried him through. Sooner or later he had to cope with the numerous cases in which the crystal offers no perfect plane of cleavage. This is so in copper sulphate, for example, and to make matters more difficult the crystal exhibits no right angles. Now whenever a crystal does show cleavage the fractures are parallel to certain of its faces. Haüy therefore felt justified in selecting the well-developed faces *p*, *M*, *m* (of Fig. 8) as defining the walls of his fundamental cell (Fig. 9), and thereby got a structure in complete agreement with all known facts (Fig. 10).

The value of a scientific theory is most strikingly vindicated when its predictions come true. Crystals of " blue vitriol " have since been studied in at least four European Universities —Bologna, Cambridge, Munich, and Petrograd—the combined results being the observation of 24 facets unknown to Haüy. They are all parallel to important planes of his cell-structure or " lattice," and the angles they make with each other could have been computed beforehand if he had thought it worth while.

The answer to any question concerning the nature of a crystal must therefore take the form that it is a uniquely regular and static type of structure made possible by the abstraction of heat from more mobile states of aggregation. Rock-salt and copper sulphate simply represent the two extremes of this cellular structure: a rectangular cell with equal edges and a skew parallelepipedon respectively. Lying between them are various types of cell, but these need not be enumerated. A growing crystal generally exhibits plane boundaries (a fortunate circumstance, no doubt, as otherwise the nature of the interior could scarcely have been guessed); but this is an effect and not a cause, for some crystals offer curved surfaces during growth, and all lose their sharp edges and corners during the inverse process of dissolution.

The *X*-Ray Proof

Such results as the foregoing seemed to justify a belief that a crystal is an orderly arrangement of atoms or molecules, *i.e.* of particles so minute as to defy the resolving powers of the strongest microscope. The fine-spun threads of the space-lattice therefore run through the whole fabric of crystallographic effort and achievement, but the theory remained intangible until the year 1912, when an infinitely refined experimental method was presented to the world by Laue. Much had happened in the 125 years succeeding Haüy's first published work. The theory of crystal structure had been repeatedly elaborated and refined (especially by Wollaston; Frankenheim and Bravais; Sohncke, Fedorov and Schoenflies; Barlow, Sollas and Hilton). The theory and practice of spectrum analysis, including the optical effects produced by diffraction gratings and piles of thin plates, were well understood. Atoms had been distinguished from molecules, and had been weighed, both relatively and in absolute measure. *X*-Rays had been discovered by Röntgen, and shown by Barkla to defy every convention of chemical combination. Many facts connected with radioactivity had been recorded by Becquerel and the Curies, and proved by Rutherford and Soddy to be due to a spontaneous disintegration of certain atoms; and finally Rutherford had gauged the effect of α-particles on matter, evidently rehearsing (as we have since learned) the part of Macaulay's New Zealander—though it is the Empire of the indivisible " Atom " that is in Ruins.

It was about this time, then, that the splendid idea occurred to Laue that Haüy's three-dimensional grating might solve the question whether *X*-rays are corpuscles or electro-magnetic

undulations of short wave-length. Provisional estimates had placed the magnitudes concerned in X-rays and crystal lattices at one ten-thousandth of those involved in the more familiar visible spectra and ruled gratings; so an experiment seemed called for and was actually effected by Friedrich and Knipping. The apparatus used is shown in Fig. 11, where A is the anticathode of the X-ray tube, $B_1 - B_4$ are diaphragms allowing a narrow beam of rays about 0·75 mm. diameter to fall on the crystal, K, adjusted on a goniometer, G. Photographic plates were placed in such positions as $P_4 - P_5$ and treated to a very long exposure. The first crystal tried was copper sulphate, and the result is given in Fig. 12, which indicates that secondary beams are set up in the crystal, and diffracted away from the primary pencil. A coarsely powdered aggregate of crystals revealed the somewhat different pattern of Fig. 13, the object being to show that the general effect is independent of any particular circumstance of normal incidence at a crystal boundary. Different crystals gave different patterns; moreover, the symmetry of the photograph is related to the direction of the primary beam, as illustrated by Figs. 14 and 15, giving the results obtained from cube and octahedral plates of zinc-blende.

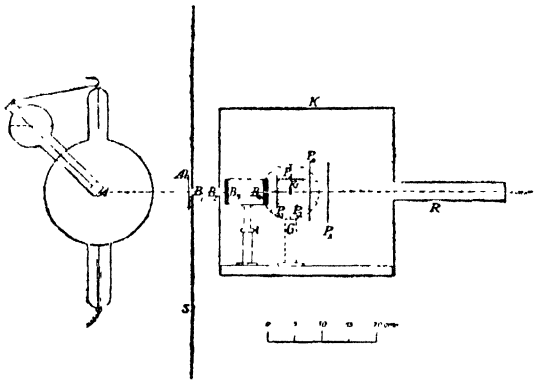


FIG. 11.—X-RAY APPARATUS USED BY LAUE, FRIEDRICH AND KNIPPING.

Laue's theoretical explanations were precise and exhaustive, after the manner of the mathematical physicist.

So brilliant a discovery naturally attracted the attention of practical physicists, especially in this country. The younger Bragg (W. L.) introduced a most fruitful mode of interpretation, each spot of the photograph being referred to a cumulative reflection at internal plane layers of atoms. The crystal, then, was regarded as a pile of parallel plates, the " thickness of the plate " being the perpendicular distance between the successive atomic layers; and the simple equations ($\lambda = 2d \sin \theta$, $2\lambda = 2d \sin \theta \ldots . n\lambda = 2d \sin \theta$), already known to hold for ordinary wave-lengths, optical thicknesses, and angles of incidence, were found to apply to the smaller magnitudes concerned. An acute analysis of the Laue radiograms justified the inference that zinc-blende has a particular type of structure (different from Laue's), the nature and dimensions of which accounted perfectly for every spot of the radiogram.

Equally satisfactory results followed from W. L. Bragg's investigation of several other cubic crystals, partly by the original method of Laue and partly by a new method of precision, that of the X-ray spectrometer, devised by his father, W. H. Bragg. Considerations of space,

unfortunately, rule out any detailed description of these cases (as also of those partly or wholly investigated by W. H. Bragg), but an exception must be made in favour of rock-salt. The result is to vindicate Haüy's fundamental cubical cell in every respect, for atoms of sodium and atoms of chlorine are alternately arranged at the corners as shown in Fig. 16. Moreover, by taking into account the specific gravity of rock-salt and the known absolute atomic masses of sodium and chlorine, it was possible to compute the absolute size of the cell. Its edge-length is $2{\cdot}814 \times 10^{-8}$ cm. Further, since the cell depicted obviously constitutes the smallest conceivable fragment of rock-salt, the conclusion may be drawn that four molecules, 4NaCl, represent the minimum amount of matter involved in the creation of a crystal. But such a crystal would not be apprehensible by any known method of investigation. Its volume might have to be augmented a million-million times before it could be tested by any known method.

It must now be mentioned that, in most preceding conceptions of the structural cell, the corner-particles have been treated as quite small, since it was desirable to emphasise the fact

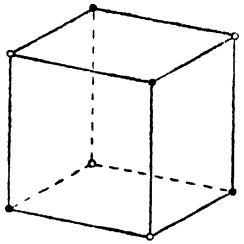


FIG. 16.—W. L. BRAGG'S ROCK-SALT STRUCTURE.

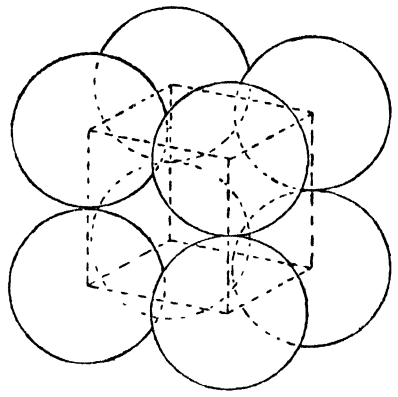


FIG. 17.—ROCK-SALT STRUCTURE WITH ATOMS EXPANDED INTO CONTACT.

that it is the regular nature of the atomic arrangement that really matters, and not the actual size of the atoms. Now atoms have presumably certain volumes of influence which actually touch in the crystal; and possibly the most interesting recent development of *X*-ray work is that it gives us a method of estimating these "atomic diameters." The structural cell of rock-salt should accordingly rather be conceived as resembling Fig. 17, in which the atoms have expanded themselves so as to occupy most of the cell-space.

It now behoves us to return to copper sulphate—the historic substance initially selected by Laue for his crucial experiment. Is the present-day knowledge of this crystal at all comparable with that of the cubic rock-salt? A little reflection will show that this is not to be expected. Consider a better-known province: that of organic chemistry. The chemist knows quite well the molecular structure of methane or tartaric acid, or benzene, or even of some of the simpler sugars and alkaloids; but not of many others of greater complexity. Possibly he has only been able to isolate them in a state of purity, and determine their empirical composition and molecular weight. He hopes to solve such complex problems as his powers increase; and so it is with the *X*-ray worker. The Laue experiment showed that copper sulphate is an unsymmetrical crystal—which is the sum total of *X*-ray knowledge concerning it.

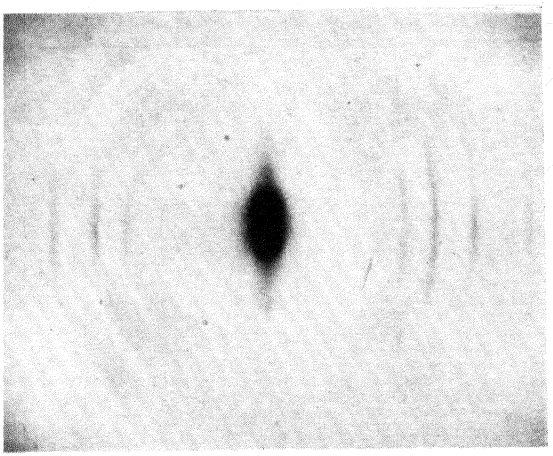


FIG. 18.—SPECTRUM OBTAINED BY PASSING *X*-RAYS THROUGH PLATINUM FOIL (*after de Broglie and Lindemann*).

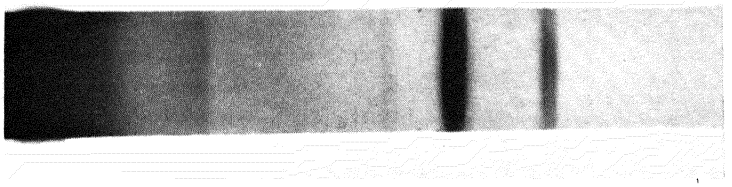


FIG. 19.—PART OF THE PREVIOUS FIGURE SHOWING GREATER DETAIL.

Its "crystal percentage composition" (shape and dimension of the fundamental cell) have not been determined. Nor has the "crystal molecular weight"—whether the average mass placed at a corner of the cell is half the molecular weight as in rock-salt, or the molecular weight itself, or a small multiple of the molecular weight. Such values are actually determinable at the present moment even if the substance be so complicated as cane-sugar or cryptopine. But this would only be the beginning of an *X*-ray investigation, the goal of which is not to determine the centres of gravity of groups of atoms, but the position of every atom throughout the structure. The situation is quite different in such simple crystals as fluor-spar or calcite, for the atomic positions are to a large extent defined by "symmetry," and the rest can be deduced by a careful comparison of intensities of reflection. Perhaps the high-water mark of these purely *X*-ray determinations of structure is represented by W. L. Bragg's recent work on aragonite, the rarer modification of calcium carbonate.

There is, finally, an intermediate type of crystal exploration, namely, that which depends on *X*-ray angles for the cell dimensions; recognises the problem to be too complex to be usefully illuminated by intensities; and falls back on other sources of information for the position of the various atoms. Notable examples of this type are to be found in Astbury's recent work on tartaric and racemic acids; and in Sir W. H. Bragg's investigations of such aromatic compounds as benzene, naphthalene, and anthracene; from which it appears that the molecule or closed rings of the chemist can be fitted into the cells defined by the *X*-ray spectrometer. In principle, such developments represent an advance, for the molecular configurations of the organic chemist, having had a long start, are in a much higher state of development than the atomic dispositions of the *X*-ray analyst; but they leave much to be desired in matters of detail, for there are generally alternative ways of packing formulæ into cells. This state of affairs is quite inevitable, but not necessarily permanent.

In conclusion, let us not miss the furthest consequence of the *X*-ray method of exploring crystal structure. Classical geometrical studies imply a definite surface of macroscopic dimensions. Not so the new method, for the effect is purely internal, and the smallest visible crystal represents a million undulations of *X*-rays. The latter was first strikingly shown by de Broglie and Lindemann, who sent a beam of rays through a piece of platinum foil (an aggregate of invisibly small crystals) and thereby obtained the characteristic series of spectral lines of Figs. 18–19. The same method was adopted two years later by Debye and Scherrer and independently by Hull, and the technique so improved that the "powder method" is giving excellent results. What is even more startling is that the *X*-ray method can be usefully applied in the direction of non-crystalline materials (certain "liquid crystals"), for it merely premises regular layers of matter in tune with its minute wave-lengths.

Moseley's Crystal *

W. H. and W. L. Bragg's pioneering work on crystal structure took a further direction, namely, the determinations of *X*-ray wave-lengths. Following up a suggestion by C. T. R. Wilson, they had found that crystal faces also give intense reflections at successive angles

* The historic crystal of potassium ferrocyanide, $K_4FeCy_6,3H_2O$, as actually mounted by Moseley, forms one of the exhibits. It is, perhaps, not unworthy of mention that the crystal exhibits two facets, *o* ($1\bar{1}1$) and *x* ($13\bar{1}$), not hitherto recorded in the literature, and that it is an aggregate of fine twinned components (as is almost always the case with this substance).

demanded by the equations, $\lambda = 2d \sin \theta$, $2\lambda = 2d \sin \theta$, and so on; and as the factor d was known for their standard rock-salt crystal, it was only necessary to determine the angles of intense reflections in order to evaluate the wave-lengths. It was thus found that the wave-length of X-rays depends on the composition of the anticathode, in so far as the metals platinum, palladium, rhodium, and tungsten are concerned.

Now experiments in the same direction were being independently carried out by Moseley and Darwin, who were therefore in a position to confirm the results on platinum anticathodes, and with added precision. Further, the extension of the work to all available chemical elements led Moseley to the discovery of simple relations between the order of the elements and their characteristic X-ray wave-lengths—a discovery which is generally regarded as of greater funda-

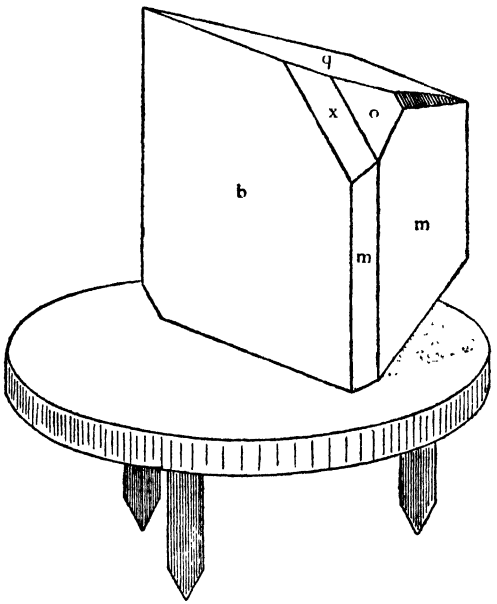


FIG. 20.—MOSELEY'S CRYSTAL OF POTASSIUM FERROCYANIDE, MOUNTED FOR USE WITH THE X-RAY SPECTROGRAPH.

mental importance than any other result of X-ray investigation, demonstrating as it does that atomic properties are defined by the nucleus charge or " number " rather than by atomic weight.

The crystal used by Moseley throughout the whole of this work was a fine specimen of the " monoclinic " potassium ferrocyanide, some 6 cm. square, of which Fig. 20 is a faithful reproduction. The largest face, b, was used as the grating. This gave an especially intense " third-order reflection " ($3\lambda = 2d \sin \theta$), which was accordingly adopted as giving results of treble accuracy (a comparison with the standard rock-salt crystal gave a grating distance $d = 8{\cdot}454$ Ångström units). The work involved great experimental difficulties, which were all finally overcome; and an examination of all available elements from aluminium (No. 13) to gold (No. 79), revealed a regular march of wave-lengths in both of Barkla's K — and L — series of radiations—but with three gaps, which were attributed to elements unknown to the chemist.

Perhaps the most important result of Moseley's work, the justification of atomic number

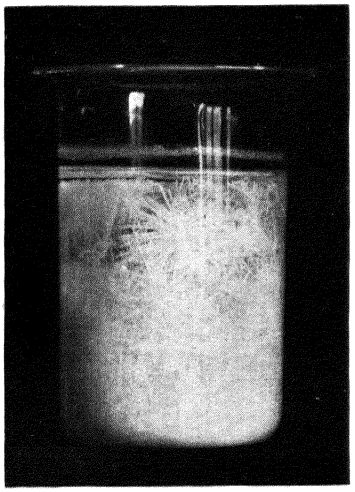


FIG. 21.—CRYSTALLISATION OF *p*-BROMACETANILIDE IN THE FORM OF BULKY RADIATING NEEDLES.

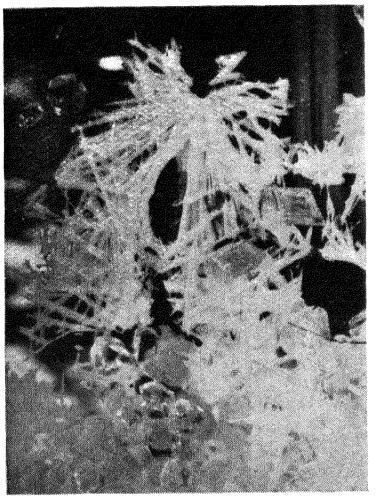


FIG. 22.—THE FIRST APPEARANCE, TWO DAYS AFTERWARDS, OF THE COMPACT MODIFICATION.

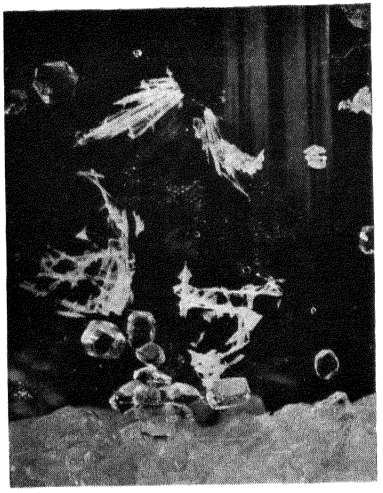


FIG. 23.—GRADUAL PROGRESS OF THE COMPACT VARIETY.

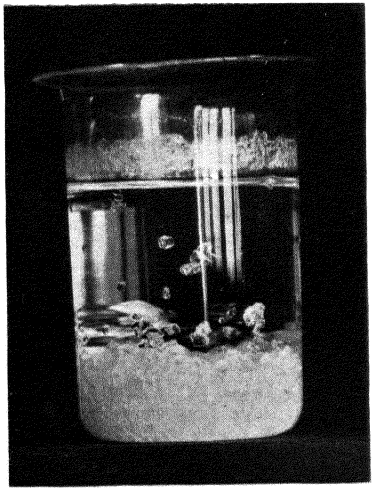


FIG. 24.—FINAL STAGE OF THE CRYSTALLISATION.



FIG. 25.—ETHYL AZOXYBENZOATE (WITH A LITTLE ROSIN) BETWEEN CROSSED NICOLS: CONICAL VARIANT OF THE SMECTIC TYPE OF STRUCTURE. MAGNIFICATION ABOUT 18 DIAMETERS (*after Friedel*).



FIG. 26.—ETHYL ANISALAMINOCINNAMATE SHOWING THE FAN STRUCTURE OF THE SMECTIC TYPE. MAGNIFICATION ABOUT 18 DIAMETERS (*after Friedel*).

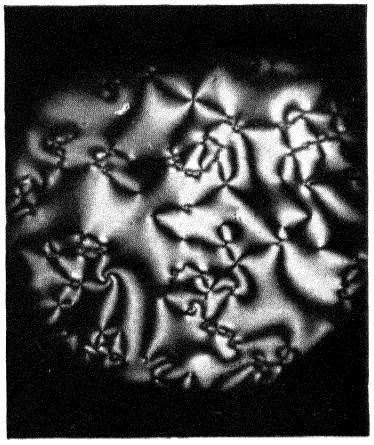


FIG. 27.—AZOXYPHENETOLE (WITH A LITTLE ROSIN) BETWEEN CROSSED NICOLS: NUCLEAR VARIANT OF THE NEMATIC TYPE OF STRUCTURE, THE NUCLEI BEING CONNECTED BY DARK BANDS. MAGNIFICATION ABOUT 55 DIAMETERS (*after Friedel*).

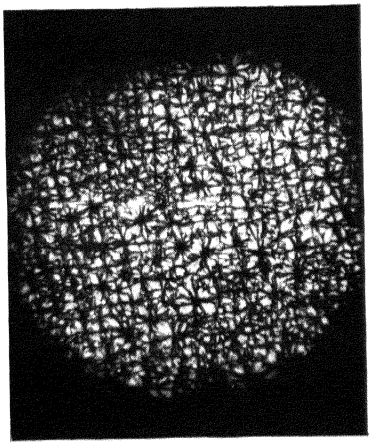


FIG. 28.—CHOLESTERYL BUTYRATE BETWEEN CROSSED NICOLS: CHOLESTERYL FAN STRUCTURE OF THE NEMATIC TYPE. MAGNIFICATION ABOUT 55 DIAMETERS (*after Friedel*).

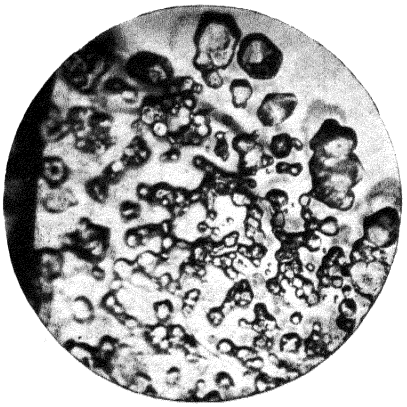


FIG. 29.—IRREGULAR GROWTH OF CÆSIUM SULPHATE ON POTASSIUM SULPHATE (× 25).



FIG. 30.—PARALLEL GROWTH OF CÆSIUM SULPHATE ON RUBIDIUM SULPHATE (× 25).

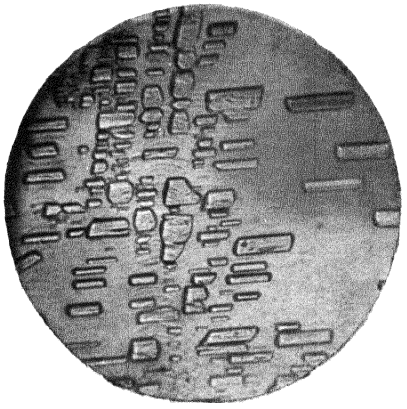


FIG 31.—PARALLEL GROWTH OF RUBIDIUM CHROMATE ON SULPHATE (× 100).

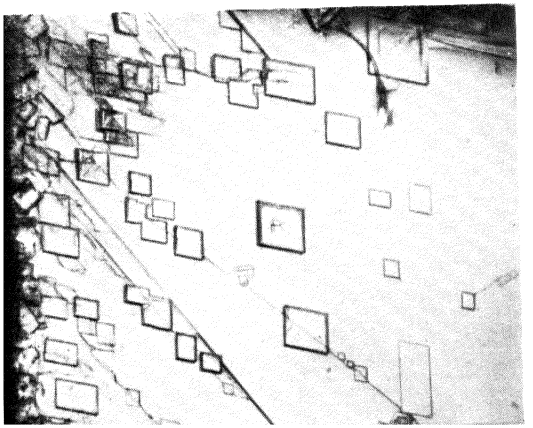


FIG. 32.—REGULAR GROWTH OF SODIUM NITRATE ON A CLEAVAGE SURFACE OF CALCITE (× 25).

as a fundamental property, lies outside the scope of this paper; but there are two others of supreme value which require emphasis. The first is that it removes the anomalies exhibited by certain elements, when arranged according to atomic weights; thus cobalt and nickel, tellurium and iodine were first placed by *X*-ray wave-lengths in the order demanded by their chemical properties.

The second result is not less weighty, at any rate to the crystallographer. On account of their liquid or gaseous nature, certain elements are obviously unsuitable for use as anticathodes, but Moseley found that their compounds served equally well for his purpose. Potassium chloride, for example, was used for getting the lines both of potassium and chlorine; and oxides were used in place of rare-earth metals. The immediate inference is that *X*-rays are a sub-atomic property, and throw no light on the external valency electrons which provide an occupation for the chemist. All crystal reconstructions by the *X*-ray method are therefore purely stereophysical.

As Moseley points out, some of his materials betrayed the presence of impurities by revealing corresponding additional lines. Thus his cobalt contained nickel; and his nickel, manganese. He therefore suggested that his method might prove useful in chemical analysis, one advantage being that *X*-ray spectra are much simpler than ordinary optical spectra. The method " may even lead to the discovery of missing elements, as it will be possible to predict the positions of their characteristic lines "—a prophetic remark in view of the recent discovery of Hafnium.

Polymorphism

Of the two provinces of polymorphism (crystal and liquid) the former is more familiar to the chemist. Obscurely explored by early mineralogists, it was definitely annexed by chemistry in the person of Mitscherlich, and surveyed in turn by Frankenheim, Lehmann, Ostwald, and van't Hoff. The recent systematic researches by Tammann and Bridgman at low temperatures and high pressures, as also of Chattaway and his co-workers under more ordinary conditions, demonstrate with certainty that nearly all substances can solidify in two or more crystal modifications. As has been shown by Chattaway, a warm alcoholic solution of *p*-bromoacetanilide, for instance, crystallises in interlacing or radially arranged needles, completely filling the vessel as a felt-like mass (the radial structure, so common in the " pitch stones " of the petrologist, is clearly seen at the upper part of Fig. 21). Then a more compact and less soluble form makes its appearance and gradually works its way down, " consuming " the needles, and generally leaving a dense layer of large crystals at the bottom of the vessel (Figs. 22–24).

Amongst the classical cases of polymorphism may safely be reckoned diamond and graphite, white and grey tin, and calcite and aragonite. They have all been subjected to scrutiny by *X*-rays and been proved to have different lattices, as expected. Even more instructive are the two cubic forms of ammonium chloride, as they only differ in density and refractive index. Their structures also are now fully known and suggest the desirability of a new term, " many-structured."

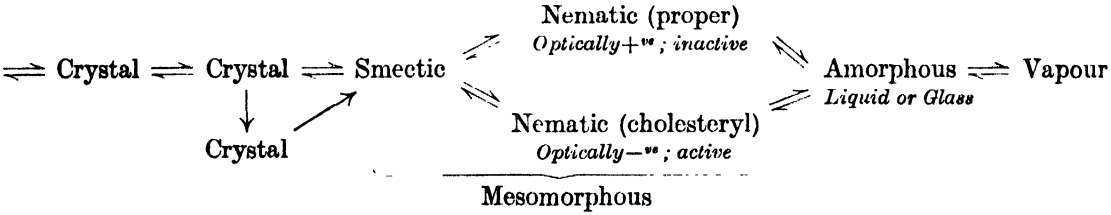
A similar observation might appear to be devoid of all meaning if applied to the province of liquids. How can a liquid substance exhibit different structures? Are not all liquids structureless or amorphous? Such, of course, was the general view before the year 1888, in which Reinitzer published the observation that cholesteryl benzoate melts to a turbid liquid, which on heating becomes quite clear. The immediate history is fairly well known, for although

many hard things have been said of Otto Lehmann, it has never been urged that his pen ran dry. The term "Liquid Crystals" was almost inevitable in view of their novelty and strong double refraction.

The present century has witnessed some remarkable developments. Profiting by the technique created by Lehmann, many workers have applied themselves in turn to the elucidation of this baffling problem. First came the organic chemist Vorländer, bringing gifts in the shape of four hundred new examples of doubly refracting liquids, with constitutions which would seem to indicate an elongated type of molecular configuration. To him is also due the important generalisation that the liquids all belong to the uniaxial type of double refraction. Then came the physicists Bose and Mauguin, who independently showed that the application of a strong magnetic field serves to orientate the various parts of a cloudy liquid into a clear but still doubly refracting fluid. The subsequent researches of Mauguin, Grandjean, and Friedel were mainly directed towards the study of fine structure and of the orientative action exerted on the liquids by fresh cleavage surfaces of real crystals.

Then came the inevitable *X*-ray examination, which appears to have been first applied by van der Lingen to *p*-azoxy-anisole and *p*-azoxy-phenetole, but with negative results (since confirmed by others). This, however, was not allowed to be a final answer, for it had been made almost certain by Friedel that, however varied may be the external shapes, there are in reality two and only two types of anisotropic liquid structures, namely, the "smectic" (soapy) and the "nematic" (fibrous), the cholesteryl type being a variant of the latter, endowed with enormous rotatory power (up to 36,000° for 1 mm. thickness) by virtue of a twisted structure (Figs. 25–28). This brilliant anticipation has been lately verified by de Broglie and Friedel, jun., who have found that the pasty smectic sodium oleate consists of plane or curved parallel strata of a constant thickness equal to 43·5 Ångström units, each layer of the structure freely gliding between its upper and lower neighbours. The nematic phases, on the other hand, are presumably Bose's mobile sheaves of fibres, free to move in every direction, whilst preserving a parallel orientation, and therefore without any special action on *X*-rays.*

The complete property of polymorphism may therefore be summarised after Friedel as follows:



with sharp transition temperatures at every junction. It is only necessary to contrast this with the early nineteenth century scheme, crystal ⇌ liquid ⇌ vapour, in order to estimate certain rates of progress.

* It might be worth while to be on the look-out for a third type of structure, intermediate between the smectic and crystal structures, and conceivably represented by a crystal in a process of flow through an orifice under the stress of unilateral pressure. The structure in mind would reveal several series of *X*-ray lines, emanating from a group of strata having a common zone-axis.

Isomorphism

The fundamental fact that closely related substances are not literally "isomorphous," but differ from each other by small angular values, had been established some years before Mitscherlich left school. Wollaston, for example, had proved the rhombohedral carbonates to differ from each other by as much as 2° and Haüy had differentiated celestine from barytes by measurement some 20 years earlier. It is clear that Mitscherlich's first impression of absolute identity was not founded on measurement; but as he subsequently corrected it by the use of a Wollaston goniometer, and also made most comprehensive investigations in this province, he is rightly regarded as the discoverer of isomorphism.

The modern period may well be dated from the work of Retgers, who not only established the important straight-line relation between density and percentage composition of isomorphous mixtures, but also applied it to the elucidation of isodimorphous mixtures, proving beyond all doubt that one substance can force a second, closely related to it, to take up its own form and structure in a state of what van't Hoff would have called "solid solution."

Another important series of researches we owe to Tutton, whose systematic work on the geometrical, volume, optical, and other physical properties of potassium, rubidium, and cæsium compounds has just been completed. The investigations are perhaps especially notable on the optical side, for they involved the designing and construction of several new instruments of precision including a cutting and grinding goniometer, which allows of the preparation of orientated parallel-plates and 60°-prisms, with an error as low as two minutes of arc. The result of this work—extending over some 45 compounds belonging to the single and double sulphates and selenates of the types R_2SO_4 and $R_2SO_4,RSO_4,6H_2O$—has been to show that the properties vary regularly with increasing atomic weight of the alkali metal. Moreover, similar investigations on some 30 corresponding ammonium and thallous salts have revealed an astonishing closeness in angles and volumes to the rubidium compounds.

It seems certain that this work will be constantly drawn upon when the time comes to correlate the physical properties of a crystal with its intimate structural details. A commencement of this correlation has, in fact, already been made by Born, Madelung, and others for the elastic properties of cubic crystals; and also by Professor W. L. Bragg, who informs me he has succeeded in establishing a quantitative connection between the optical properties of calcite and aragonite, and their fine structure as revealed by *X*-rays.

Isomorphous substances have also been investigated in other directions, all in harmony with a conclusion that their mutual affinities are rigorously circumscribed by volume-relations. If the molecular volumes be sufficiently close, two such substances respond to tests on the formation of mixed crystals, regular alignments or parallel growths on one another and the relief of supersaturation of each other's solutions. These results are mainly due to the Russian crystallographer Wulff and to a series of workers in the Oxford Laboratory. Potassium and cæsium sulphates, for example, will neither form mixed crystals nor induce a parallel orientation on each other (the growth of Fig. 29 is seen to be quite irregular); whilst all other possible pairs make the fullest response in both capacities. Similar results are obtained with scores of other substances, so that the decisive *rôle* played by molecular volume would seem to be placed beyond all doubt (compare Figs. 30–34).

The significance of the volume constant is not far to seek, for it is clearly a relative measure

of the size of the fundamental cell. If the latter have a cubical shape, as in rock-salt or the common alkali halides, the distances between adjacent atoms are to each other as the cube-roots of the respective molecular volumes (as shown in Figs. 35–36).

The same idea holds with structural cells of other shapes, the relative dimensions of which were termed "topic axes" by Muthmann and Becke. It need scarcely be added that the *X*-ray method substantiates this interpretation of molecular volume, and with it the inference that corresponding atomic spacings must be reasonably close, if isomorphous substances are to mix well or influence each other in various ways.

The relation between composition and optical constants of isomorphous mixtures is evidently a subject of perennial interest, perhaps because of its growing complexity. Lavenir, for example, believed he had proved that mixtures of the two Seignette salts follow an additive law in the matter of the three principal refractive indices; but it has been pertinently objected by Wulff that such work does not decide between a proportionality according to volumes or according

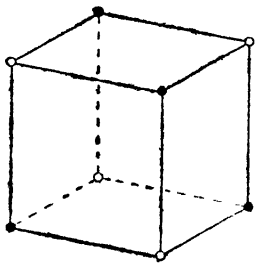


FIG. 33.

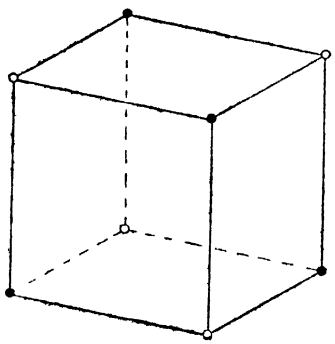


FIG. 34.

STRUCTURAL CELLS, DRAWN TO SCALE, OF ROCK-SALT AND RUBIDIUM IODIDE.

to weights. Wulff's own work at first pointed to the first contingency, but his later investigations would seem to negative either conclusion, from the utmost refined point of view. Whether this is wholly due to perturbing inhomogeneities is not quite clear, but researches at present in progress bid fair to throw much light on this question. There is, for example, Buckley's highly significant observation that freshly prepared mixed crystals of the Seignette salts show optical anomalies, which as time goes on right themselves by a spontaneous process of annealing; and a painstaking four-years' series of investigations by Miss Porter points a general truth that mixed crystals are rarely free from structural irregularities.

Any discussion of mixed crystals would be far from complete if it failed to take account of "pseudo-racemates." The discovery of these substances by Kipping and Pope naturally created great interest, and if they have lately sunk into the background, it is simply because their properties were so well investigated at the outset that little was left to subsequent workers. Strictly speaking, they are, of course, enantiomorphous, and not isomorphous, mixed crystals, consisting as they do of intercalated *d*- and *l*-material. This intimate mixing is apparently not so easily effected as with isomorphous constituents, for the angles differ considerably from those of either component.

The above summary may have seemed to indicate that possibilities for "isomorphous"

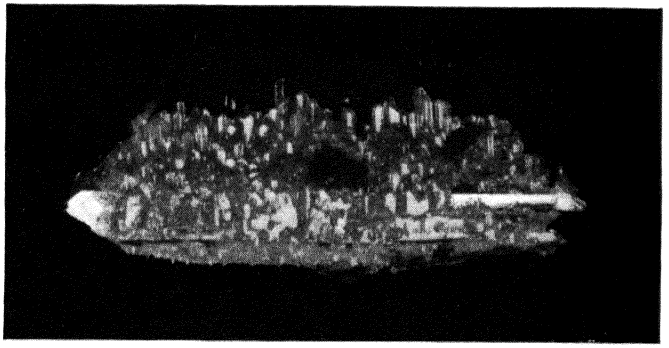


FIG. 35.—REGULAR GROWTH OF POTASSIUM PERCHLORATE ON A CRYSTAL OF BARYTES.

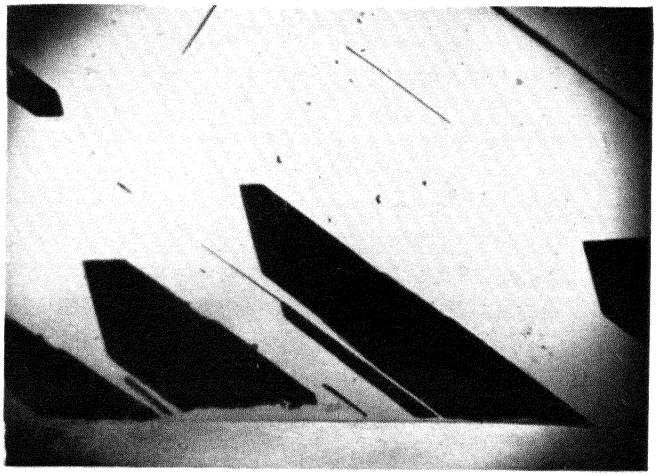


FIG 36.—REGULAR GROWTH OF POTASSIUM PERMANGANATE ON A CLEAVAGE SURFACE OF BARYTES (× 100).

researches are becoming a little attenuated—a conclusion which might appear to be supported by any appeal to the province of organic chemistry, for Boeris' azobenzene and stilbene and Jaeger's *p*-nitroso-dimethyl- and -diethyl-aniline here stand out as lonely examples. But even negative results can have valuable implications. The general absence of isomorphism amongst carbon compounds, especially, be it noted, in members of an homologous series (as recently emphasised by Miss Porter), reinforces a conclusion that molecular structures must not merely be similar but almost congruent if they are to exhibit crystal analogies. A brief return now to the inorganic domain may not be devoid of profit—at any rate, if it be accompanied by a strengthened belief that any display of isomorphism does imply deep-seated molecular affinities.

The great majority of isomorphous inorganic compounds follow the lines of the periodic classification, one or more atoms being replaced by others without any apparent change of valency. To quite a different category belongs the classical case of sodium nitrate and calcite, a frequent subject for disputes, which were all the more fervid because high principles were at stake. Can two substances be isomorphous which are unable to form mixed crystals, however easily one arranges itself in parallel position when grown on a crystal of the other? Alternatively, is there any reason for doubting the correctness of the alleged dissimilarity of chemical constitution? As the latter possibility always seemed unthinkable, there could obviously never be any question of a recognition *de jure chemicali*, but only one of *de facto crystallino*.

The position has recently been somewhat modified by the recognition of many examples of a similar nature by the present writer and by Langmuir. Thus, the alkali perchlorates, permanganates, and borofluorides not only exhibit all the subtle geometrical peculiarities of the barytes group of minerals, but also furnish magnificent specimens of parallel overgrowths, in so far as differences of molecular volume will allow.

Any such multiplication of examples naturally brings into the foreground questions of constitution. Is there any way of drafting really isomorphous formulæ in accordance with the state of the substances in the crystals? The constitution in the liquid condition is not necessarily relevant. Apparently the only way out of the difficulty is to apply Werner's ideas on co-ordination, and resolve the salts into "ions" on the following lines:—

$$Na^{+}[NO_3]^{-},\ Ca^{++}[CO_3]^{--},\ Mg^{++}[CO_3]^{--};$$
$$K^{+}[ClO_4]^{-},\ K^{+}[MnO_4]^{-},\ K^{+}[BF_4]^{-},\ Ba^{++}[SO_4]^{--};$$

in which the ionised parts are premised to take up regular positions in the crystal by virtue of electrostatic forces. Those who are practised in locating electrons will find them isomorphously distributed. In any case, it will be observed that such formulæ offer a common interpretation of the old and new types of isomorphism. That they are also in harmony with the behaviour of crystals in the infra-red region is an additional cause for satisfaction.

So far as *X*-rays are concerned, it need only be said that they bring nothing but confirmation of the views held by crystallographers. The new method may therefore be confidently applied to the exploration of such cases as crystallise badly, but with the important proviso that all results should be confirmed by the older methods; for isomorphism implies something more than approximate equality of structural cells as revealed by similar spectra, namely, a correspondence in the chemistry and symmetry of the crystals, both of which lie outside its ambit.

Optical Activity and Enantiomorphism

Pasteur's memorable separation of sodium ammonium "racemate" into *dextro-* and *lævo-*tartrates is generally allowed to be an event of far-reaching importance. In the first place, it gave a fortunate biological bias to all his subsequent work, ranging through studies of fermentation to methods of combating disease in living organisms. Secondly, it harvested a ripe body of knowledge, relating to optical activity in liquids and enantiomorphism of crystals, and sowed the precious seed in the chemical molecule—a fertile soil which has since produced the vigorous plant of stereo-chemistry. The third result is even more important, so far as the study of crystals is concerned, for reasons which will now be made apparent.

The province of crystal structure has always suffered from an unfortunate polarisation, inasmuch as it is only explorable on the physical side. Any successful attempt to permeate a crystal with a chemical reagent could only lead to its destruction. Direct chemical action has accordingly to be restricted to mild surface agencies, and much has to be learnt in this way. The only other possible chemical methods of investigation must rely on properties which survive a state of liquefaction. It is in this direction that Pasteur's work acquires a unique importance. The absence of any racemisation effect in the reversible process, optically active liquid $\rightleftharpoons$ crystal, proves each of three propositions: the chemical molecule persists in the crystal; the molecule is enantiomorphous all the time; and, therefore, the crystal structure is eternally enantiomorphous.

Now it is even more obvious that atoms persist in every chemical compound, gaseous, liquid, or crystal, and the question may well be asked: Is it not a little invidious to select Pasteur's work and place it on a crystal pedestal? The answer lies in the circumstance that enantiomorphism is inseparably related to that property of "symmetry," which is of greater importance in the province of crystals than in any other domain of science.

It was realised quite early in the nineteenth century that the external symmetry of a crystal is limited by the lattice-nature of its structure to 32 kinds or classes. Further, that there is a symmetry-limitation to the property of enantiomorphism, for no finite body can differ from its mirror-image, if it have a plane or centre or alternating axis of symmetry; and, inferentially, that only 11 of the 32 classes are inherently enantiomorphous. But the division of crystals into the 32 classes is a counsel of perfection, owing to the general circumstance that a crystal does not usually reveal its true symmetry by any single property. Crystals are therefore more practically grouped into seven systems (each containing a certain number of classes) by such properties as are easily investigated.

The general consequence is that the symmetry of most crystals is imperfectly known, the principal exception being the optically active group, for the symmetry limitations are here so stringent that the true class of symmetry follows immediately from a few angular measurements. The Pasteur Principle, then, raises such crystals on to a higher plane of certainty, so that optical activity may be regarded as a true patent of nobility, equally recognised in every Court of Aggregation.

The determination of optical activity is frequently beset with great difficulties in the crystalline condition, for it can in general only be detected along directions of single refraction or "optic axes." Pocklington's work on cane-sugar accordingly acquires a real historical importance, the more so as it brought the first proof that a biaxial crystal may have different

rotatory powers, even of opposite sign, along the two "singly-refracting" directions. The optical scheme is given in Fig. 37, in which the values refer to thicknesses of 1 cm. Neither value is identical with what might be expected from the study of solutions, but this disagreement, it must be added, has no connection with "mutarotation," the obvious interpretation being that the solution-value is a statistical effect, whilst the crystal values represent rotations along definite directions of parallel molecules.

Further support to the above interpretation came from Pocklington and Dufet's work on the two Seignette Salts (the tetrahydrated sodium ammonium and sodium potassium *d*-tartrates). In both substances the rotatory power is necessarily identical by symmetry along the two optic axes, but the value in one salt is quite different from that of the other (although the atomic structure must be practically identical), and is even of opposite sign. The cause for this apparently strange behaviour lies in the totally different orientations of the optic axes—along which rotatory power has, perforce, to be measured—in the two salts, as

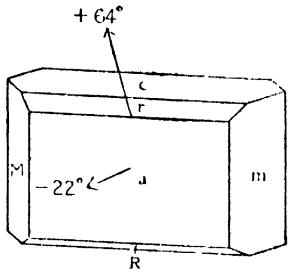


FIG. 37.—CANE-SUGAR SHOWING THE TWO DIRECTIONS OF SINGLE REFRACTION.

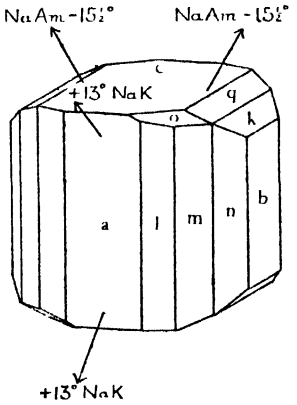


FIG. 38.—THE SEIGNETTE SALTS ILLUSTRATING THE DIFFERENT OPTICAL DIRECTIONS WITH CONSEQUENT DIFFERENCES OF ROTATORY POWER.

shown in Fig. 38. The *l*-tartrates have not been investigated, but would undoubtedly behave in an inverted manner.

The angle between the two optic axes of a biaxial crystal may vary greatly for different colours, and in some cases become zero for a particular wave-length, and in such a way that the resulting single optic axis is normal to a large face. Advantage of this has been recently taken by Greenwood in showing that triphenyl bismuthine chloride is optically active in the crystalline condition.

The question now arises how far the *X*-ray method supports the Pasteur principle that all optically active substances have enantiomorphous structures; and it seems advisable to begin with those substances which preserve their activity in the dissolved condition, as being more interesting to the chemist. Apparently the only substance of this class that has been examined in both *d*- and *l*-forms is triethylenediamine cobaltic bromide, $[Co\ en_3]Br_3 2aq.$ which has been investigated by Jaeger and Haga by the Laue method. The radiograms are identical in every respect, and exhibit planes of symmetry. Many other substances have been examined by the same authors in one form only, including such historically important substances as sodium

ammonium tartrate, tartaric acid and cane-sugar. All appear from the radiograms to possess one or more planes of symmetry.

It is therefore evident that the *X*-ray method is incapable of revealing structural enantiomorphism, and that its elucidation in any doubtful case is not to be expected. The same conclusion holds for substances which only exhibit optical activity in the crystalline condition. Quartz, cinnabar, sodium chlorate, and zinc sulphate, for example, have all been examined by Haga and Jaeger and found to behave as if the structure were identical with its mirror-image.

Now such results as the above had already been predicted by Friedel from a critical examination of the first Laue radiograms, some of which relate to crystals, which, although incapable of enantiomorphism, belong to relatively low types of symmetry. A case in point is zinc-blende, the radiogram of which exhibits a symmetrical repetition of a four-fold character, instead of the two-fold repetition demanded by the true crystal symmetry (Fig. 14). Friedel's generalisation takes the form that the reaction of a crystal to *X*-rays is " centro-symmetrical," which means that crystals of some classes may appear to have a higher symmetry than they really possess. The 32 classes of crystal symmetry are thereby telescoped into 11 groups (which should not be confused with the 11 enantiomorphous classes, however much each is derivable from its analogue by adding a centre of symmetry); and as each *X*-ray group covers at least two crystal classes, there is a riot of ambiguity.

Such a state of affairs is not altogether unexpected, as the crystallographer has long been acquainted with similar cases. It is, however, not the less instructive, as indicating once more that purely physical and purely chemical properties are but partial aspects of an harmonious physico-chemical whole. The future welfare of the science is evidently bound up with a more perfect attainment of the homogeneous phase at the common boundary of the two great provinces of knowledge. Unfortunately, this does not seem to be possible at the present moment in the crystal interior. All the greater reason, then, for a brief survey of the physico-chemical boundary, which separates a growing or dissolving crystal from its solution.

Crystal Growth and Dissolution

The normal product of crystal growth is a surface bounded by plane faces intersecting in straight edges, any proper investigation of which correspondingly implies measurement of two kinds: (1) plane, or edge angles, and (2) interfacial. Now both kinds were determinable by the " contact goniometer " of Delisle and Haüy (as illustrated by Figs. 39 and 40 for a crystal of quartz), but the instrument suffered from two real disadvantages. A crystal of fair size is needed, and the results cannot be depended upon to parts of a degree (1°).

The introduction of a reflecting goniometer * by Wollaston (1809) got over both difficulties, and placed the first instrument of precision in the hands of the crystallographer (Fig. 41). Its use led to a general revision of Haüy's angular data, but established all the more the principles underlying his work, for although angles were now found to fluctuate over a range of some 40′ their average values fitted admirably with his theory of structure.

The mechanism underlying these fluctuations of angles remained quite unknown until the subject was taken up by Miers, who devised the inverted form of goniometer of Fig. 42, which

* Wollaston's own goniometer forms one of the Exhibits, by the kindness of his great-nephew, Mr. C. Hyde Wollaston.

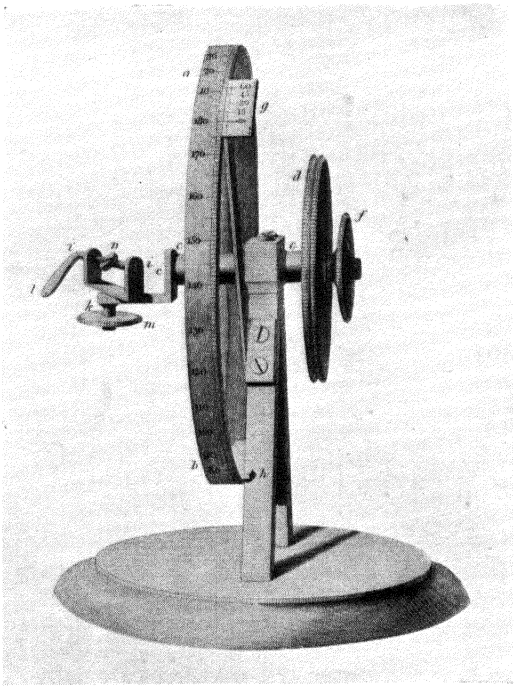


FIG. 41.—WOLLASTON REFLECTING GONIOMETER.

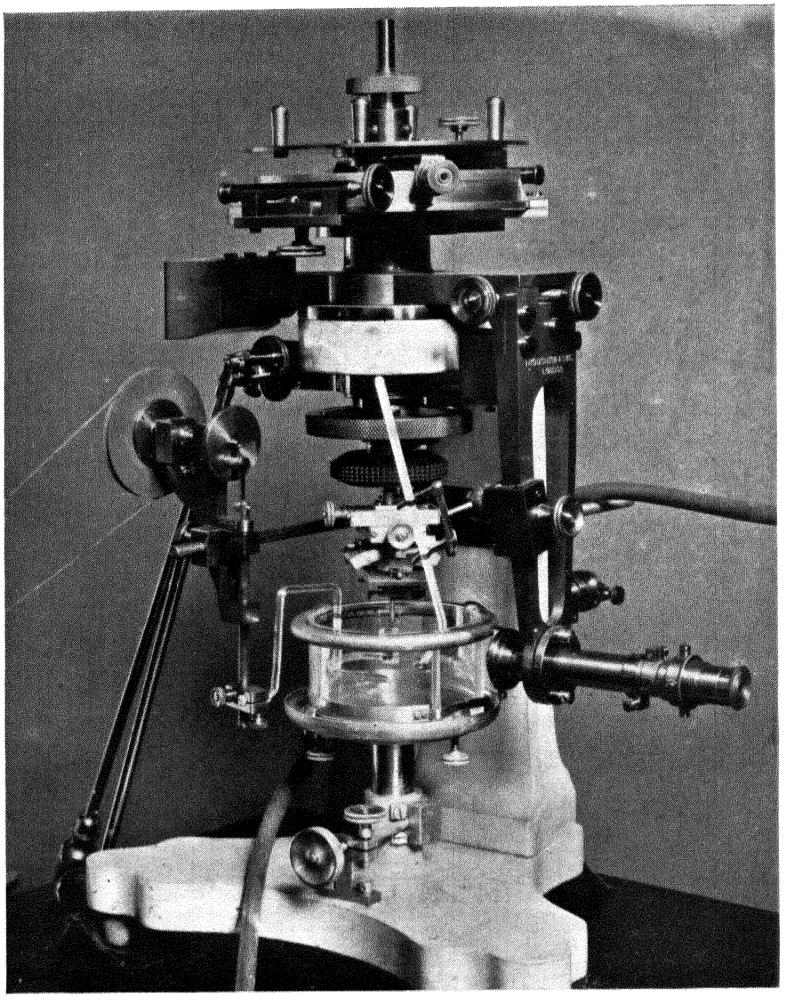


FIG. 42.—MIERS' INVERTED GONIOMETER.

allows a continuous process of measurement whilst the growing crystal is immersed in its solution. It was thus found that no face remains parallel to itself during growth, but alters its direction at intervals in a discontinuous way, sometimes, as in the case of alum, resolving itself temporarily into a group of three " vicinal " faces. The oscillatory movements of the growing faces were

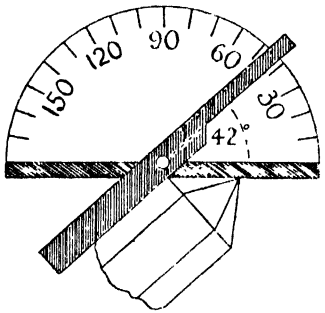


FIG. 39.

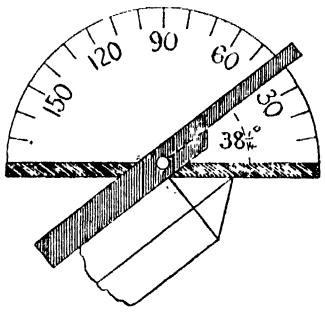


FIG. 40.

CONTACT GONIOMETER ADJUSTED TO MEASURE EDGE-ANGLE AND INTERFACIAL ANGLE, RESPECTIVELY, OF A QUARTZ CRYSTAL.

ingeniously referred to a process of escape of water molecules from the crystal boundary. It will be realised that the actual angular values given by any crystal depend on an accidental factor, namely, the moment at which it happens to have been taken out of the solution under the ordinary conditions of the laboratory.

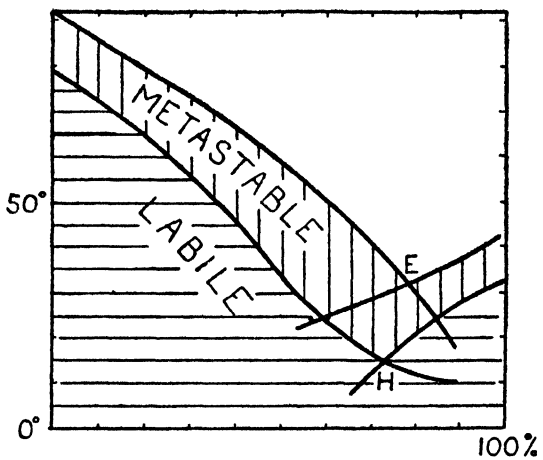


FIG. 43.—FREEZING AND SUPER-FREEZING POINT CURVES OF MIXTURES OF SALOL AND BETOL.

Such results naturally led to a further enquiry, that concerning the nature of a solution in immediate contact with a growing crystal. Is the solution just supersaturated? Alternatively, are there various types of supersaturation, each recognisable by unmistakable properties? In a series of investigations, in collaboration with Miss F. Isaac, it was shown, by measuring

the refractive index of the solution in contact with the crystal, that there are two degrees of supersaturation, the metastable and the labile. A solution in the former condition will not crystallise spontaneously, however violently stirred, but will quietly deposit material on any crystals that happen to have been introduced. A solution in the labile state, on the other hand, immediately liberates a shower of crystals on shaking, the result being a sharp drop in the refractive index.

The generality of these conditions of supersaturation is convincingly proved by the behaviour of binary mixtures of such organic substances as salol and betol. In addition to the ordinary freezing-point curves meeting in the eutectic point, *E*, of Fig. 43, it was possible to map out parallel super-freezing-point curves and a hyper-eutectic point, *H*, the first series giving the temperature–concentration relations for a crystallisation in presence of solid nuclei, and the latter series referring to the behaviour of mixtures when unassisted by such incentives to crystallise.

The metastable and labile conditions can co-exist in different parts of a drop of solution. This is illustrated in the photomicrograph of Fig. 44, in which the " large " crystals of potassium bichromate are a result of quiet growth from a metastable solution. Sooner or later this is followed by a rapid separation of branching needles from the labile state, and the two processes may alternate until the last portion of water has evaporated.

It is now convenient to return to the Wollaston goniometer. This type of instrument can only be applied to measurement in the sense of Fig. 40 (p. 73), and not of Fig. 39 in which the contact goniometer is applied to a pair of edges (prism and pyramid); and its intrinsic worth can scarcely be more significantly estimated than by the rapidity with which it was generally adopted. In view of the accuracy of the interfacial angles, crystallographers were quite content to adopt them exclusively, and deduce edge-angles by processes of calculation, which were rendered less laborious by the methods of Miller.

Apparently the first to realise the want of a more general type of instrument of precision was Miller himself, who some time in the 'seventies combined two instruments in such a way that both kinds of angles could be measured; but as the object he was investigating (a faceted bead of platinum) revealed a chaotic (non-crystalline) assemblage of faces, he dismantled the instrument and left a few notes of his work, which were eventually published by his successor, Professor W. J. Lewis.

Two-circle goniometers were first openly introduced some twenty years later. The only really workable type appears to be that independently designed by Fedorov and Goldschmidt, and sufficiently illustrated by the original Fedorov goniometer of Fig. 45. The telescope is provided with auto-collimation. The crystal (say of quartz) is mounted and adjusted on the vertical circle, and can be further rotated about the axis of the horizontal circle, by means of which two movements any face can be brought into the reflecting position. Both circles are read in each position, one giving edge-angles, the other interfacial.

The primary object of the two-circle goniometer was to explore plane surfaces, more accurately and expeditiously and without the wholesale repetitions so disingenuously betrayed by long tables of single-circle readings (some two-thirds of which have no practical value or influence on the final accuracy of the work). But the instrument also opens up a new province of work, namely, the investigation of curved surfaces, occasionally developed on growing crystals and always produced when a crystal dissolves.

Now it is almost axiomatic, in any portrayal of character, that the straight line of the cubist

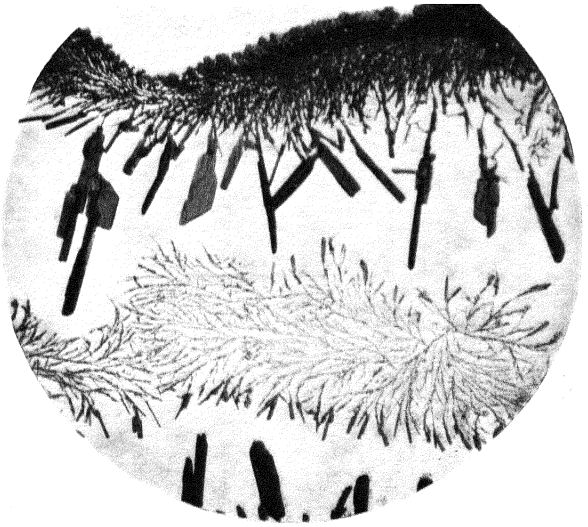


FIG. 44.—POTASSIUM BICHROMATE SHOWING METASTABLE AND LABILE STAGES OF CRYSTALLISATION.

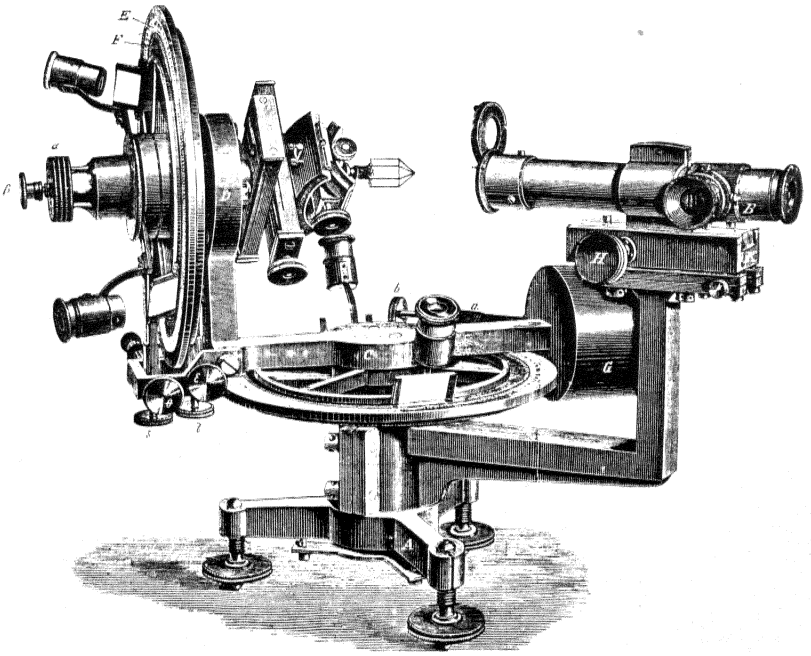


FIG. 45.—THE ORIGINAL FEDOROV TWO-CIRCLE GONIOMETER.

is less certain than the artist's curve. Small wonder, then, that this truth can be read from the world of crystals. The character of a crystal: the way in which it responds to an external stimulus: in a word, its symmetry, is more surely revealed by curved than by plane facets. Of course straight lines (and plane faces) have their value, indicating as they do directions (or layers) of atoms, but their number and disposition frequently fall short of informing us about the finer organised details. The curved edge or surface, on the other hand, is susceptible of infinite variations, each revealing something of value to the sympathetic observer.

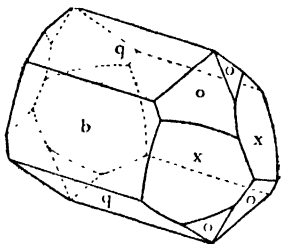


FIG. 46.

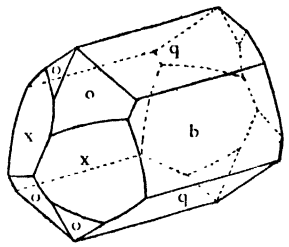


FIG. 47.

CRYSTALS OF ACID CÆSIUM *l*- AND *d*-TARTRATE SHOWING ENANTIOMORPHOUSLY ARRANGED CURVED SURFACES.

Consider, for example, the two crystals of Figs. 46 and 47. They would be absolutely identical were it not for the curved elements of surface, x, tetrahedrally arranged. As they actually stand, a mixture could be separated into two kinds by the help of a two-circle goniometer, and separately examined in the polarimeter. They happen to be crystals of cæsium acid tartrate (*lævo* and *dextro*), so the result is a foregone conclusion; but in principle, they might have been a new substance, "X," under investigation by the chemist.

The behaviour of calcite during a process of dissolution teaches the same lesson. If a

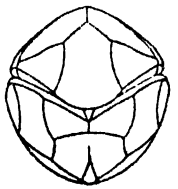


FIG. 48.

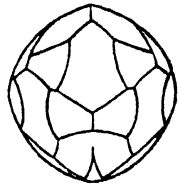


FIG. 49.

FORMS ASSUMED BY A SPHERE OF CALCITE WHEN PARTIALLY DISSOLVED BY DILUTE ACID (*after Goldschmidt and Porter*).

sphere be first cut and then rolled about in dilute acid, it passes through the form of Fig. 48, to that of Fig. 49, which it substantially preserves in later stages. Such studies as these (due to Penfield, Goldschmidt, Wright, Fersmann, and others) show how candid is the answer of the crystal to any question concerning its symmetry, provided it be put in intelligible language. If the question be asked in an unknown tongue, there is either a Sphinx-like silence or a reply so cryptic as to demand the services of a group of interpreters.

It must now be added that the two-circle goniometer is not the most general type of instrument possible, and inconvenience may rise in measurement, if the crystal under examination

be very minute. It was in order to meet such cases that a three-circle-instrument was devised by Herbert Smith. This has been "improved" by others, but with results of questionable value.

Simultaneously with the above-noted improvements in measuring instruments, attempts have not been wanting to replace ponderous methods of interpretation by rulers and compasses. It is to be feared that the only result of many graphical methods is to shed lustre on the logarithmic processes they were designed to replace. But this can scarcely be said of the methods advocated by Mallard, Fedorov, Goldschmidt, Becke, and Penfield, and of those due to Hilton, Hutchinson, and Herbert Smith in this country, all of whom would seem to have realised that simplicity is the keynote to progress.

Practical Applications

All practical applications of crystallography would seem to depend from the general truth that each crystalline substance has one or more properties, distinguishing it from all others; but so has every homogeneous liquid or vapour, and the question may be put whether the crystal offers any advantage. Of course it does. In the first place, a crystal refuses to exist in any but a refined atmosphere—a truth which is especially brought home to the organic chemist who has frequently considerable difficulties in persuading his oil or tar to crystallise; but when it does, he knows full well it is worthy of a quantitative analysis.

The second advantage is equally patent. The majority of liquids and all vapours can only give statistical answers; the crystal, on the other hand, replies in three dimensions. A liquid may have a refractive index 1·592; the same substance, when crystallised, precise values 1·563, 1·612, and 1·696 along three definite directions, mutually perpendicular. And so on with other properties, including that of form.

A further advantage lies in the circumstance that crystallographic methods lend themselves to small-scale experiments. The polarising microscope has long been a favourite engine of research, and two American workers, Hull and Kerr, are demonstrating what can be done by the powder method of *X*-ray analysis.

Crystallographic methods of identification have accordingly long been practised in many provinces of enquiry. Sorby taught the world how to create a technique serving the interests of two sciences (petrography and metallography), and others have shown in many ways how a given substance can be proved to be *A*, or *B*, or neither, by characteristic crystal properties.

Now suppose the answer be neither *A* nor *B*, and the substance be too precious or small in quantity to allow of chemical analysis; how is one to proceed? The only answer is, Consult Fedorov's "Crystal Kingdom." This is a lexicon of all published crystal descriptions arranged on original lines, permitting those who have mastered the method to find the particular substance which offers the same angles as a crystal under examination. It will be realised that the process of identification does not depend on any previous personal knowledge of the specimen under investigation. The method has already proved its value, substances so varied in composition as ammonium magnesium phosphate, calcium oxalate, and phenyl salicylate having thus been identified in the Oxford laboratory.

Sometimes Fedorov gives no reply when consulted, for there were only 7,500 substances to classify in his time. Others can be trusted to fill in cases as they are published, and possibly simplify the process. In which connection I am persuaded as a result of some three years' work

that the problem of crystal classification can be solved by methods which should commend themselves to all crystal morphologists, since they require no drastic recourse to unusual orientations. Some 300 crystals, including all the most difficult cases, have been brought into order, and only await a series of practical tests. If these prove satisfactory, the science or art of crystal identification will become open to all who can measure a crystal.

Conclusions

The peculiar occasion of the publication of this paper would seem to justify a conclusion, that citizens of the British Commonwealth of Nations need hide no diminished head where the study of crystals is concerned. There was, of course, a time when purely scientific work was necessarily confined to the Home Countries, for pioneers in new lands are constantly against the forces of Nature in the open, and not merely in small-scale laboratories. But that time is long past. All are working in friendly emulation, and apparently with equal success. Canadian and Australian mineralogists, for example, are conspiring to make it difficult for any single person to keep up with the literature. A South African is the first to apply the *X*-ray method to the problem of "liquid crystals." And so on with the others—as for the dwellers at the Antipodes, have they not a prescriptive right to hold up the mirror to Nature?

But, after all, science recognises no vertical lines of cleavage between nations, only taking note of the impervious nature of the horizontal stratum that separates those who seek Truth from those who hold they have inherited it. There is apparently a fair proportion of each kind in all countries, and a few of the former have been mentioned, all too inadequately, in these pages.

There is, however, a final inference, namely, that we still know little about certain aspects of crystals, and that we cannot hope to know much more by present-day methods. This should not be taken to imply any captious dissatisfaction with the present state of knowledge, but rather an aspiration to something higher. The physics of crystals has always been in advance of the chemistry, and is not less so since the year 1912. The chemical background, on the other hand, is somewhat dark, the only bright star in the firmament being Pasteur.

Now discoveries are not made every day, even by those from whom much is expected, so we must do the best we can until the time appointed. If history has any prospective value, there will be many which have their origin in crystals. There is, then, every reason to hope that a young investigator of the future will take a crystal of alum, and warm it at the fire of his genius; when it will glow far into the night, revealing the chemical meaning of double salts and, most wonderful of all, the significance of water, congealed by chemical forces. Then shall a fascinating province of enquiry have acquired a rounded measure of physico-chemical symmetry; and, shedding the last vestige of a "Graphic" or "Descriptive" nature, lay claim to a prouder title, Crystallology—the Science of Crystals.

X-RAY ANALYSIS OF CRYSTALS

By Sir William Bragg, K.B.E., F.R.S.

There is a strong analogy between the use of *X*-rays in the investigation of crystal structure and the employment of light in conjunction with a diffraction grating. There is, however, a very great difference in scale, for the *X*-ray waves are ten thousand times shorter than those of light. The ordinary diffraction grating consists of a sheet of metal or glass on which parallel lines are ruled, say, 20,000 to the inch. When a ray of homogeneous light is directed upon such a grating diffracted pencils of light leave the grating in various directions according to well-known rules. That which is least diffracted we call the effect of the first order, and the others are of the second order, the third order, and so on. The angles which these diffracted pencils make with the original rays are determined by two factors, namely, the wave-length of the light and the spacing of the lines on the grating. It will be possible, given a wave-length, to find the spacing by measuring the "angle of diffraction." Such a measurement is very exact. There is another well-known grating effect which is sometimes made use of. The relative intensities of the different orders but not their angles of diffraction depend upon the dimensions and form of the groove which the ruling diamond makes on the plate. Sometimes one spectrum is intensified by some particular characteristic in the forms of the groove. It might be possible to work back from observations of the relative intensities to a determination of the shape of the groove.

When we turn to *X*-rays we find the analogue of the light waves in the waves of the *X*-rays and the analogue of the grating in the ordered arrangement of the crystal. If *X*-rays are allowed to fall upon a crystal, diffracted pencils may be emitted and the angle which the diffracted pencil makes with the original depends upon the wave-length of the *X*-rays and the spacings of the crystal. There is now a new effect in that the direction of the original rays has to be related to the lie of the crystal planes in different ways before any diffraction takes place at all. In the actual experiment the crystal is rotated about some important axis until the diffracted pencil of the rays flashes out and the angle of diffraction is observed just as in the case of light.

The chemical molecule consists of a certain number of atoms arranged in an ordered way. When the molecules are built into a crystal they tend to an arrangement which has a higher symmetry than the molecule itself possesses. We may say that Nature puts together two, three, four, or even more molecules in such a way as to make for higher symmetry. In this way she makes a unit of pattern. The units of pattern are distributed on the lines and planes of a lattice, each unit having exactly the same form, composition, and outlook as every other unit: the whole structure of the crystal is an orderly arrangement of these units. They may be considered to lie on various planes or sheets within the crystal, just as the rows of trees in an orchard may be considered to lie in various rows. Each such sheet corresponds to a line in the light-grating. The *X*-rays give the distance between sheet and sheet. They may do this for sheets drawn in various ways, and hence it is possible to determine the arrangement of the units in the crystal, that is to say, the form and dimensions of the cell occupied by one unit. This measurement corresponds to the determination of the spacing between two lines in the diffracted grating. A further step which the *X*-rays can take is the determination of the relative intensities of the various orders of the diffracted rays, information which leads, if it can be interpreted, to a knowledge of the mutual arrangement of the molecules in the crystal. This operation, which is always carried out in the case of *X*-rays as far as present experience will allow, is analogous to a determination of the form of the grooves of the diffraction grating by measuring the relative intensities of the various orders of diffracted light. Two stages may therefore be distinguished in this process.

One of them comparatively easy: the other of difficulty and sometimes of very great difficulty.

The outer form of a crystal depends upon the internal arrangement of the atoms and molecules. It is possible to distinguish thirty-two different classes each characterised by its own special form. Mathematical crystallography has carried the possibilities of classification further than the outward form can reveal. Taking any group of atoms, it has shown that in each class having its special external characteristics there are several ways of arranging the groups so as to give the same outward appearance. It may be said at once that the group employed by Nature is in general the chemical molecule. These different methods of arrangement are nearly always distinguishable from one another by their action on the *X*-rays. There are in all 230 of them. An early result of the *X*-ray analysis is, therefore, the determination of the special arrangement of the molecules within the crystal. The *X*-rays are not absolute masters of this analysis, but are nearly always successful with some little assistance from observation on the outside form.

The next stage, the more difficult one, is a determination of the full linear and angular relations between the position of the molecules and the atoms within the molecules. The aids to this determination are relative measurements of intensities of diffraction as revealed by *X*-rays, to which must be added all that may be known of the chemical and physical and mechanical characteristics of the atoms and the molecules. In some simple cases the analysis may be said to be already complete, but in the hundreds of thousands of known crystals there is of course an immense field still to be covered.

It will now be convenient to refer to some of the principles of structure which analysis has already revealed. It is clear that such principles are to be looked for carefully as throwing light on chemical and physical actions and also as helping to further determinations of crystal structure. There is, in the first place, a broad division into different methods of combination between the atoms. Three types are to be recognised. The first of these is illustrated by such crystal structures as rock salt, fluorspar, calcite, and so forth. The structure depends mainly upon a group formed in obedience to laws of electro-static action. If, for example, we take the case of rock salt, the chlorine atom has taken away from the sodium atom one electron which it has incorporated into its own structure. According to the modern views of atomic constitution, the chlorine atom, which has seven electrons in its outermost electron shell, is eager to complete the shell—completion implying the presence of eight electrons in that shell. Neon, which has actually eight, seems to show by its unwillingness to enter into chemical combination—in other words, by its unwillingness to give, take, or share electrons—that there is something which makes the eight a satisfactory and complete number. Sodium has the completed outer shell of eight, and one which is the beginning of a new shell external to the old. It appears to have a poor hold on this odd electron, so that chlorine easily removes it. In consequence, the chlorine becomes a negatively charged body, and the sodium a positively charged body. Each positive surrounds itself with as many negatives as possible, and each negative with as many positives as possible. The cubic structure of rock salt is obtained in this way, each atom having six neighbours of opposite sign. In fluorspar, where the calcium atom has been robbed of its two extra electrons by two fluorine atoms, each of which takes one, Nature has found a structure in which the positively charged calcium is surrounded by eight negative fluorines, and the fluorine by four calciums. In Iceland spar the same principle governs the structure. Each calcium atom is surrounded by six CO_3 groups and each CO_3 group by six calciums. The structure is not, however, so regular as

rock salt, because the CO_3 group is not spherical in form and characteristic. A very large class of crystals is built on the same plan. There is a certain indefiniteness about the molecule, because a positive can be associated with any one of the six negative neighbours which it possesses. It is notable that in calcite the CO_3 group must have such a degree of symmetry as is represented by the properties of an equilateral triangle. If it is turned round 120 degrees in its own plane, it has the same appearance as before. This implies that the three oxygen atoms are all alike in their relations to one another, and to the other atoms of the crystal, however the crystal may come to pieces under chemical action. The crystal is a compound of calcium atoms and CO_3 groups, but not a mixture of CO_2 and CaO. It is supposed that the carbon atom is stripped of all the four electrons which it normally possesses in its outer shell. The calcium atom loses also the two electrons which it has outside its completed shell, and each of the oxygen takes two of the six electrons thus set free. Consequently each carbon atom has a quadruple positive charge, each oxygen a double negative charge, and the calcium a double positive charge.

A second method of combination is to be found in the diamond. The carbon atoms of which it alone consists are so arranged that each carbon has four neighbours arranged about it in tetrahedral fashion. Each shares two electrons with each of its neighbours, and in this way covers itself with the desired shell of eight electrons. It appears that the sharing produces a very strong bonding; the diamond is the hardest of known substances.

In graphite there are sheets of atoms tied to one another by the sharing bonds of the diamond, but these sheets are separated from one another by a considerable interval. In this way may be explained the slipperiness of graphite and its usefulness as a lubricant, because in the first place the layers slip on one another easily, the bonds that tie them together being weak, and in the second place, the atoms in each layer hold tightly together. There are indications that these tight bonds are much less affected by temperature than bonds of a looser type. For example, the coefficient of expansion with heat of the diamond is far less than the average expansion of graphite, but the expansion of graphite takes place almost entirely through increased separation of the layers.

There is yet a third method of combination, in general much weaker than the other two. When molecules, as in organic crystals, are built together into a structure, the forces that bind together molecule and molecule may be comparatively weak. The separate molecules are not positive or negative to each other, nor do they share electrons, but no doubt there are stray fields, perhaps electric, perhaps magnetic, at different points on their surfaces which cause the molecules to be joined on to one another like the girders of an iron bridge. The crystal structure is very empty, like lace work in space. We get the first hint of this lightness in the diamond, where the empty spaces are big enough to accommodate as many more carbon atoms as a diamond already contains. The root principle seems to be that the carbon atom, when sharing electrons, gathers round it four neighbours more or less at the corners of a tetrahedron. If these points of attachment are spaced, so to speak, over the surface of the carbon atom, it is easy to understand how these open structures can be formed. In the diamond crystal, the structure shows two types of arrangement which form the basis of two of the great groups of organic substances. There is in the first place the hexagonal ring which appears to be capable of separate existence in unchanged form and dimensions, and when fringed with various atoms of radicals to form the innumerable members of the aromatic series. The double and treble rings are found in naphthalene and anthracene respectively and the structure of these crystals as revealed by *X*-rays

shows that the ring is the same in all respects as in the diamond. There is also to be found in the diamond an arrangement of long chains of carbon atoms, which chains may have any length. These chains, when fringed along their length by hydrogen atoms and finished off at each end with various groups such as CH_3, the methyl group, COOH, the carboxyl group, OH, the hydroxyl group, and so on, form the well-known chain compounds of organic chemistry. Measurements of the lengths of these chains have recently been made very exactly by the *X*-ray method in a number of cases, and it appears that the arrangement is, as the models show, just the same as is found in the diamond. The essential feature is that any two carbon atoms joined on to a third lie at points on the surface of the latter, which are tetrahedral points.

The application of the *X*-rays to the crystal analysis of metals has shown very remarkable results which will probably receive great extension in the future. Many of the metals—aluminium, silver, copper, and gold, for example—are of a structure which implies the simplest form of close packing of spherical atoms. These plates are those in which the packing is most dense. A mass of crystals is stronger than a single crystal, because the planes of weakness lie in all directions. An admixture of a certain number of foreign atoms causes a distortion of the structure which diminishes the possibility of slip, and thus the hardening effect of an alloy is explained.

In the case of steel, it seems likely that the carbon atoms do not replace iron atoms, as, for example, tin atoms replace those of copper in the formation of bronze, but fit into the interstices of the structure. The structural nature of the various crystals which form in alloys, as, for example, cementite in steel and intermetallic compounds in other alloys, have also been the subject of investigation.

Among the many other developments to which *X*-ray analysis is leading, one more may be mentioned. It now seems possible to calculate, from a knowledge of the structure and of the atoms which compose it, the effects upon electro-magnetic waves, such as those of light, on their way through the crystal. A beginning in this respect has been made with the measurements of the refractive indices of calcite and aragonite.

THE RARE GASES OF THE ATMOSPHERE

By Morris W. Travers, F.R.S.

A century and a half ago, mainly as the result of the investigations of British chemists, certain knowledge of the nature of the atmosphere first began to dawn. Within a few years it was definitely established that air consists chiefly of the gases which we now call oxygen and nitrogen, in the invariable proportion of 21 volumes of the first to 79 volumes of the latter. Air could be deprived of oxygen, leaving nitrogen as a residue; and oxygen had been prepared from sources other than air, the artificial oxygen being found to be identical in its properties with the gas existing in the atmosphere.

In 1785 the English chemist Henry Cavendish described before the Royal Society experiments which are the starting point of the story now to be told. He found that when electric sparks were passed through air a change took place, described in modern language as combination of the oxygen and nitrogen. If a solution of potash was placed in the vessel through which the sparks were passed, nitre was formed, and if the sparking was continued for long enough the air volume continued to diminish till all the oxygen had disappeared, some of the nitrogen being left. If more oxygen was added, and the sparking continued, further contraction took place; and at last there was left only oxygen, which could be absorbed by a solution of *liver of sulphur*, leaving, however, a small quantity of gas which could not be made to diminish in volume on prolonged sparking with fresh oxygen.

Cavendish's experiments contain the germ of two important discoveries. By a process analogous to the sparking of air in presence of potash or lime-water, carried out laboriously by means of a primitive electric machine, vast quantities of nitrate are now manufactured. That there is in air a small quantity of gas which cannot be made to combine with oxygen remained unconfirmed for over a hundred years. The rediscovery of this fact opens this story.

A century after the publication of these discoveries it was universally supposed that the residue of gas obtained by removing oxygen, carbon dioxide and moisture from air was nitrogen, identical with the gas obtained by chemical processes from such compounds as ammonia. This supposition was based upon no experimental evidence, and Cavendish's experiment had been entirely overlooked.

In 1893 the late Lord Rayleigh communicated to the Royal Society a paper in which he showed that the weight of a litre of nitrogen obtained from air was 1/230 heavier than that of a litre of nitrogen obtained from a purely chemical source. In a letter to *Nature* he asked for suggestions from chemists as to the reason for this curious anomaly, but his letter met with no reply. He was inclined to the view that either the chemical or atmospheric nitrogen contained some modification of nitrogen itself. He therefore carried out some experiments to ascertain whether this was actually the case. At this stage Professor (later Sir) William Ramsay, K.C.B., asked and obtained permission to carry out some experiments on atmospheric nitrogen.

The experiments consisted in passing atmospheric nitrogen over red-hot magnesium, with which the nitrogen combined, forming a solid nitride. The residual gas was weighed in a glass bulb, and the result of the first experiment, completed in May, 1893, showed that the gas became denser, or heavier after treatment. This was encouraging; whatever substance made atmospheric nitrogen heavier than chemical nitrogen could be concentrated in the gas by treatment with red-hot magnesium. By prolonged treatment by this process the volume of nitrogen was continually reduced till about 1 per cent. of the original gas remained. Further treatment reduced the volume no further, and the density of the residual gas, compared with that of the original nitrogen, was now as 19 is to 14.

Lord Rayleigh and Professor Ramsay had from the outset kept one another informed of the progress of their experiments. At the meeting of the British Association at Oxford in August, 1894, they described the result of their experiments, and it must be admitted that their announcement met with criticism. Chemists refused to believe that an unknown substance had so long awaited discovery, literally under their very noses. Working in co-operation, but independently, the two investigators now proceeded to develop their discovery. Lord Rayleigh repeated Cavendish's experiment, and subjecting air mixed with oxygen to an electric flame in presence of potash, obtained about 2 litres of *argon*, as the new gas was called. Professor Ramsay, treating large quantities of atmospheric nitrogen with red-hot magnesium, obtained a lesser quantity of the gas. In both cases, the residual gas had a density approaching 20, compared with 14 for nitrogen.

Prior to the work of Rayleigh and Ramsay, nitrogen had been commonly regarded as a very *inactive* substance, one that would not readily take part in chemical change. As a matter of fact, nitrogen is not chemically inactive at all. The new gas, argon, was subjected to treatment by every imaginable process, chemical and physical, but no change could be brought about in it, nor could it be made to combine with other elements or compounds. It was an *inert* element, a new phenomenon in nature.

It was of first importance to fix its position amongst the elements, by determining its atomic weight. Gases are conceived as consisting of small particles, molecules, containing one, two, or more atoms, or ultimate particles. According to the view first put forward by Avogadro, and now supported by abundant evidence, the same volume of any gas, under the same conditions, contains practically the same number of molecules. In other words, all gaseous molecules, under the same conditions, occupy practically the same space. If, therefore, we know how many atoms there are in the molecule of a particular gas, and we also know the density of the gas in terms of density of hydrogen = 1, we can determine its atomic weight in terms of the atomic weight of hydrogen = 1. We have then

	Density × 2.	No. of Atoms in Molecule.	Molecule.	Atomic Weight.
Hydrogen . . .	1 × 2	2	1 + 1	1
Nitrogen . . .	14 × 2	2	14 + 14	14
Oxygen . . .	16 × 2	2	16 + 16	16
Argon	20 × 2	1	40	40
Mercury . . .	100 × 2	1	200	200

The numbers of atoms in the molecule can be calculated from the results of measurements of the rate at which sound travels through the gas. The measurements and calculations are really very simple, but the reasoning cannot be gone into here. We shall return to the question of the atomic weight later.

In these investigations much use is made of spectrum analysis. The gas is contained in a tube under low pressure, and an electric discharge is passed through it. The light emitted by

the gas is examined through a prism, and characteristic bands or lines indicate the character of the gas.

The final results of their joint investigation were made public at a meeting of the Royal Society on January 31st, 1895. On March 25th of the same year Professor Ramsay communicated to the Royal Society the discovery of another new gas. His attention had been called by Mr. (now Sir) Henry Miers to a statement of Dr. Hildebrand, that certain uranium-containing minerals, and particularly cléveite, yielded nitrogen on treatment with acids. A sample of cléveite was treated with acid, and the gas obtained from it, after purification by sparking with oxygen over potash, was placed in a vacuum tube and examined spectroscopically. The spectrum was compared with that of argon and it was at once evident that a new gas was present. The new gas was provisionally named krypton. A tube of it was sent to Sir W. Crookes for more exact spectroscopic examination.

A day or two later the result of the examination was received by telegram in the words "krypton is helium."

The following is the explanation of the wording of this telegram. In 1868 M. Janssen had observed in the spectrum of the sun's envelope during an eclipse a line which nearly coincided with the lines (D_1 and D_2) attributable to sodium vapour. In the same year, Sir N. Lockyer and Professor Frankland observed the same line, and being unable to find its equivalent in the spectrum of any known terrestrial element, suggested that it was due to the presence in the sun of an element which they called helium. Sir W. Crookes's measurements showed that one of the principal lines in the spectrum of the new gas coincided with the helium line in the sun's spectrum.

Professor Ramsay invited Professor Norman Collie and Dr. Morris Travers to join him in working out the details of the new discovery. The investigation occupied about two months, and the results were communicated to the Chemical Society in June. It was found that the density of the gas (hydrogen = 1) was approximately 2, as helium, like argon, was monatomic; its atomic weight was 4.

The two new elements,

Helium, atomic weight 4, and
Argon, atomic weight 40,

formed a class apart from other known elements in that they appeared to be completely inactive chemically. They appeared to occupy definite places in the general system, and following the analogy of known series of elements possessing similar properties, it at once appeared probable that they were also members of a series of which at least one, but probably several members, remained to be discovered. Indicating the atomic weight of the elements by the numbers below the names, we may represent the known and unknown series by:

Hydrogen.	Helium.	Lithium.	Beryllium.
1	4	7	9
Fluorine.	Unknown A.	Sodium.	Magnesium.
19	20	23	24
Chlorine.	Argon.	Potassium.	Calcium.
35·5	40	39	40
Bromine.	Unknown B.	Rubidium.	Strontium.
80	82	85	87
Iodine.	Unknown C.	Cæsium.	Barium.
127	130	133	137

Early in the year 1896 Sir William Ramsay and Dr. Travers commenced a systematic search for the missing elements, which occupied altogether nearly five years. Every possible source was investigated. The gases obtained by heating a large number of minerals were examined, as were gases obtained from mineral springs in different parts of the world. An attempt to separate both helium and argon into components by the process of diffusion, and by other means, yielded negative results.

There still remained a possibility that the missing elements might be present in minute quantity mixed with argon or helium, though previous experiments had shown that each of those gases contained, mainly, only a single substance. It was therefore decided to prepare about 15 litres of argon, in those days a very large quantity, and to submit it to a more searching test than had previously been possible.

At that time the researches of Dr. W. Hampson on the liquefaction of air had for the first time brought liquid air within the reach of scientific workers. It was proposed to liquefy the argon, and by evaporating the liquid and collecting successive quantities of the gas given off from it, to separate it into more or less volatile constituents, were such present in the original gas.

While the preparation of the argon was in progress, towards the end of May, 1898, Dr. Hampson brought to the laboratory at University College, London, a vessel containing liquid air. A few experiments were carried out with it; the balance of the liquid was allowed to evaporate freely, and the gas from the last few drops was collected for examination. The gas consisted mainly of oxygen, the more volatile nitrogen having evaporated from the liquid. After removal of the oxygen, the residue was treated for removal of nitrogen, when a residue was obtained which, like argon and helium, was chemically inactive.

The spectrum of the glow from the gas under the electric discharge showed that though the gas consisted mainly of argon it contained another new gas in no small quantity. The spectrum showed brilliant lines in the yellow and green region which were absent from the spectra of helium and argon. The sample of gas when weighed in a glass bulb was found to be denser or heavier than argon. It was clear that the gas occupying the position B or C in the table (p. 84) had been found. The new gas was named krypton.

A few days later, the large quantity of argon was ready for investigation, and the gas was liquefied in a glass bulb cooled with liquid air. When the whole of the gas was liquefied, a small quantity of gas was allowed to escape from the bulb into a special container, and this gas, containing the most volatile part of the argon, was then examined. Under the electric discharge the gas glowed flame colour, the spectrum showing that it consisted of argon together with a hitherto unknown gas. The gas was lighter than argon, and was therefore assigned to position A in the table. It was named neon.

Further examination of the argon–krypton mixture showed that at least one other and heavier new gas was present in it, and this gas was called xenon.

By this time it had been proved that a series of five " rare " gases actually existed,

Helium.	Neon.	Argon.	Krypton.	Xenon.
4·0	20·2	39·9	82·9	130·2

and these are now known to have the atomic weights given below the names, but only their positions in relation to other elements could then be indicated. The separation of these elements from one another, and the investigation of their properties occupied a full two years.

The separation of the heavier gases was conducted in the following manner. Whenever liquid

air was obtained, the gas from the last traces was collected, and the residue, after removal of oxygen and nitrogen, was carefully stored. A quantity of this gas was liquefied in a glass bulb cooled in liquid air. The more volatile argon was first allowed to evaporate from the bulb, the gas from the less volatile part, which was rich in krypton, being collected separately. When this gas had been collected, a very minute quantity of substance remained in the bulb, which only volatilised when the bulb was removed from the liquid air. This was xenon. The gases were further purified by repeated liquefaction and fractional evaporation, or distillation, and 20 c.c. of krypton and 3 c.c. of xenon were obtained pure.

The light gas, obtained from the large quantity of argon, contained neon, and further investigation showed that it also contained helium. It was only possible to purify the neon partially by liquefying it at liquid-air temperature, for after removal of some of the argon the residue, now rich in neon and helium, could no longer be condensed. The difficulty was ultimately overcome by using liquid hydrogen, obtained by a process worked out for the purpose. At the boiling point of liquid hydrogen (— 253° C.) the argon and neon in the mixture condensed, while the helium did not condense, as its boiling point is below that of hydrogen. From the mixture of argon and neon, which condensed at liquid-hydrogen temperature, the neon could be separated without difficulty, since the argon was absolutely non-volatile, while the neon evaporated fairly rapidly, so that the pure gas could be collected free from both argon and helium.

The result of the investigations of Ramsay and Travers, completed in July, 1898, established the existence of the five rare gases, and fixed the values of the atomic weights provisionally as in the first column below. Later experiments by others have led to revision of these results, but only to a very slight extent except in the case of xenon. The value obtained by Ramsay and Travers was, however, obtained by a measurement with a density bulb of capacity 7·1 c.c. the gas being under a pressure of 225 mm., and weighing 0·011 gram.

	R. and T.	Recent.	Impurity, R. and T.
Helium . . .	3·96	4·0	—
Neon	19·92	20·2	Trace helium.
Argon	39·92	39·9	—
Krypton . . .	81·56	82·9	Trace argon.
Xenon . . .	128	130·2	Trace krypton.

Some years later Sir W. Ramsay, in conjunction with Mr. H. E. Watson and Dr. R. B. Moore, obtained very much larger quantities of the rare gases, and subjected them to liquefaction and fractional evaporation, with a view to ascertain whether any similar element, other than those already discovered, existed in the atmosphere. The results were, in this respect, negative; but as it was possible, using larger quantities, to revise the values of the physical properties of the gases, they were of considerable value.

The discovery of the last member of the series, niton, concludes this part of the story. In 1902, Sir E. Rutherford and Professor F. Soddy, in describing the changes which take place in radium, showed that the first stage involved the evolution of a gas itself radioactive, but otherwise

resembling the rare gases. It was entirely inactive chemically, and was condensed to a non-volatile substance at a low temperature, being, generally speaking, rather less volatile than xenon.

Since the "emanation," or niton, is constantly undergoing decomposition at a fixed rate, and is also being formed from radium at a fixed rate, the quantity of niton in contact with a definite weight, say 1 gram, of radium must also be definite, and under normal conditions the volume is about $\frac{2}{3}$ cubic millimetre. A gram of radium is an enormous, almost a dangerous, quantity of that commodity; $\frac{2}{3}$ of a cubic millimetre, much less than the volume of the head of a small pin, seems an almost impossible quantity upon which to experiment. Yet with one-sixth of this quantity of gas Dr. Whytlaw Gray and Sir W. Ramsay measured the density of niton and fixed its atomic weight, the actual experimental value being

227 226 225 220 218 mean 223.

The value 222 had been anticipated on grounds identical with those on which the values of the atomic weights of neon, krypton, and xenon had been predicted so accurately.

The weight of the niton, which was contained in a minute glass bulb, was measured by means of a micro-balance designed by Dr. Steele and Mr. Grant, of the University of Melbourne. The weight of the material handled was about one-fifteen-hundredth milligram, or, in British units, one-hundred-thousandth of a grain.

This investigation, which crowns the story of the discovery of the rare gases, is one of the most brilliant pieces of experimental work on record.

The discovery and investigation of the rare gases gave great impetus to the development of new methods of research, and generally to the study of the physical properties of gases. How this came about cannot be told here, but a few words may be said about the industrial developments and the use of the rare gases in industry.

Helium has found use as a filling for thermionic valves and for gas arc lamps of the "pointolite" type. Millions of cubic feet of helium have been separated from natural gas by the United States War Department, and actually used as a filling for air-ships, for which its lightness and absolute non-inflammability render it particularly suitable. The separation of helium in quantity from natural gas in Canada has been carried out by Professor McLennan of Toronto.

Neon, under low pressure, and using a very low electric potential, emits a brilliant crimson glow. Tubes filled with neon were first used by Professor Fleming, of London, for detecting electric waves. Neon tubes are now used in the construction of illuminated signs.

Argon is manufactured from air in very large quantity for filling the well-known "gas filled" lamps. Thirty years ago argon was undiscovered, to-day it is so widely used that its use escapes comment.

Krypton and xenon find as yet no application, for they are indeed "rare gases," forming only 1/10,000 and 1/1,000,000 of the volume of common air. Yet, who shall say that industry may not some day find use for them?

THE CHEMISTRY OF CARBON COMPOUNDS

By Jocelyn Field Thorpe, F.R.S.

Introduction

The last fifty years of the Victorian era, which showed such an immense advance in scientific thought and knowledge, saw also the development of Organic Chemistry from its earliest beginnings as an empirical science, based mainly on rule of thumb and "trial and error," to its present position in the forefront of the exact sciences. Indeed, it is doubtful whether any other science, excepting possibly mathematics, can be called exact in quite the same sense as organic chemistry; for the organic chemist can do what no other man of science can accomplish, in that he can build up the molecules of his substances by means of models, he can then ask these models questions, and, subsequently, find that the answers he obtains are correct, by putting them to the test of experimental proof in the laboratory.

Although we must not suggest thereby any depreciation of the work carried out by the great master-chemists of the Continent, it is satisfactory to know that our own countrymen took their full share in the development of the science. The names of the two Franklands, father and son, Williamson, the elder Perkin and his two sons W. H. and A. G., Crum Brown, Japp, Tilden, the Armstrongs father and son, Pope, Wynne, and many others, form a list containing names which will live as long as Organic Chemistry remains a science.

During the past twenty-three years of the present century the science has advanced along lines which have enhanced its importance both from the technical and scientific standpoints. It cannot be denied that, prior to the War, many of our manufacturers were content to leave the development and exploitation of certain technical branches in the very competent hands of the Germans, but even during this period our scientific workers were not idle, and they more than held their own in scientific discovery and achievement. During the War we found ourselves without the technical means of making many substances necessary for our needs, but it is gratifying to realise that knowledge and skill were not lacking and that in a wonderfully short period of time we were able to satisfy most of our requirements. The lessons of the War were not in vain, and, as soon as practicable, a new impetus was given to both scientific and technical research. The establishment of the Department of Scientific and Industrial Research marked the beginning of an epoch which has already yielded valuable results both in technical and non-technical investigations, and the formation of the Association of British Chemical Manufacturers gave hopes of collaboration which have been fully justified. The future, therefore, is in some respects very hopeful, despite the fact that the scientific prospects of our Dyestuffs Industry are not yet clear.

Among the names of those who have contributed to the advancement of organic chemistry during the later period must be mentioned—the younger Perkin at Manchester and Oxford, and his brother, A. G., at Leeds; Lapworth at Manchester, and Robinson at St. Andrews, Liverpool, and Sydney; E. F. Armstrong and Hilditch at Warrington, and Baly and Heilbron at Liverpool; Chattaway and Sidgwick at Oxford, and Pope, Lowry, and Mills at Cambridge; Cohen at Leeds; Collie at University College, London; Crossley at King's College, London; Kipping at Nottingham; Morgan at Birmingham; Forster, Thorpe, and Ingold at the Imperial College; Irvine at St. Andrews; and Pickard in London.

In the following narrative an attempt has been made to tell the story of organic chemistry in language as simple as possible. By its aid, it is hoped that the non-expert reader may be able to understand, without much difficulty, the more specialised articles which follow.

(1) Structure

The earlier investigators into the Science of Organic Chemistry found themselves able to isolate, in a pure condition, a number of chemical substances which behaved in quite a different manner from those which were to hand, and could be obtained from the usual mineral sources. They recognised that these compounds, many of which were of considerable medicinal value, did not contain any elements other than those which they knew to be present in some of the various kinds of mineral matter of which the earth's surface is composed, such as, for example, carbon, hydrogen, oxygen, and the halogens, but it was noticed that they always occurred as products of animal and vegetable change and appeared to possess no relationship whatever with the substances from mineral sources which contained the same elements. Since, moreover, it was not found possible to prepare any compounds like them in the laboratory, they were placed in a category by themselves and called " Organic Compounds," the special branch of chemistry dealing with them being called " Organic Chemistry."

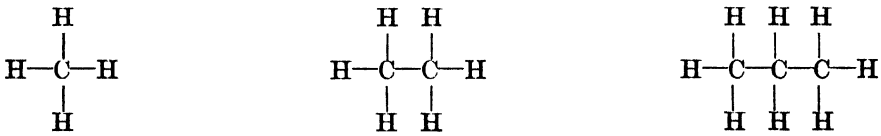
By the second decade of the nineteenth century a considerable number of these compounds had been isolated, and it was generally regarded as certain that their formation could only be explained on the assumption that some " vital force " was necessary for their production, and that, therefore, it was hopeless for a chemist to expect to obtain one of them by laboratory methods. The " Vital Theory " was propounded by Berzelius, and was held very strongly by the chemists of his time. No one offered any suggestion as to what the vital force might be, but the explanation sufficed, as such explanations will often suffice, to satisfy by means of a phrase or a formula a sense of ignorance which would otherwise have acted as a deterrent to further enquiry. It is obvious that this theory rested on the definite assumption that an " organic substance " could not be prepared in the laboratory from other than " organic " sources, and it followed that directly it could be proved that this assumption was wrong, the theory must fall to the ground. Actually in 1828 Wöhler prepared urea, a typical product of animal change, from ammonium cyanate, a compound of inorganic origin, thus giving the death blow to a theory which has since been shown to be false by the formation (synthesis) in the laboratory of a large number of plant products such as indigo and alizarin, as well as of many products of animal change, such as uric acid. Still, there can be no question that the " Vital Force " theory was right in this sense, that we are still unable to reproduce Nature's methods excepting in certain cases when we are able to use her tools, as, for example, in the conversion of a sugar into alcohol by means of an enzyme. But we do not know the method by which she works and when we have the effrontery to rejoice because we happen to have " synthesised " one of her products in the laboratory, we are compelled under cross-examination to admit that our methods compared with hers are clumsy and uneconomical in the most extreme meaning of these terms. To this extent, therefore, a vital force or mechanism is necessary for the formation of organic compounds just as Berzelius postulated.

Nevertheless, the discovery made by Wöhler had a profound influence on the development of organic chemistry, and it soon became evident that the older term had to be widened so as to include all compounds of carbon—the element which occurs in all organic compounds. The science of " Organic Chemistry " then became " The Chemistry of the Compounds of Carbon."

It is perhaps a remarkable fact that Nature should have chosen the element carbon as the basis on which she built all living matter, but a moment's thought will show that she had no other choice, and that carbon alone could give her the results she required. Carbon (atomic

weight 12), is a tetravalent element, that is to say, one atom of it combines with four atoms of hydrogen (a monovalent element), or two atoms of oxygen (a divalent element). Silicon (atomic weight 28) is also a tetravalent element, and combines in like manner with oxygen and hydrogen. Wherein, however, does silicon, which is the basis on which Nature has built most of her mineral kingdom, differ from carbon? It is this: the affinity of a carbon atom, that is, its capacity to combine with other elements, is practically completely satisfied by its combination with four atoms of hydrogen or two atoms of oxygen, whereas the silicon atom is not so satisfied. Consequently carbon dioxide (CO_2) is a stable substance, whereas all attempts to isolate silicon dioxide (SiO_2) lead to a complex form $(SiO_2)_n$ in which many units of SiO_2 are contained. Consequently CO_2 is a gas at the ordinary temperature, whilst $(SiO_2)_n$ is a rock (quartz). Another property which renders carbon the only possible element for vital purposes is its capacity for combining with itself to yield compounds having carbon piled on carbon to an apparently limitless extent.

In a compound in which the four valencies of carbon are satisfied by four hydrogen atoms it is possible to replace one or more hydrogen atoms by carbon, and to do the same with any of the hydrogen atoms in the compound formed. This process can be repeated indefinitely,



and the consequence is that one can build up long series of carbon chains in which the valencies, shown above as dashes, can be attached to either hydrogen, oxygen or some other element. The outcome is important, because, while methane (CH_4) is a gas at the ordinary temperature, the increase of molecular weight caused by the accumulation of carbon atoms leads to an increase in density, so that C_5 compounds (with hydrogen) are usually liquids and the higher members are solids. Finally, as the molecular weight still further increases the solid phase passes, yielding place to a wax-like or, as it is called, "colloidal" condition, and substances which exist in this state usually cannot be obtained in the crystalline form. In fact, the great majority of the compounds utilised by Nature are colloidal, that is to say, they are jelly-like in properties. It is evident that elements such as silicon, which form derivatives of high molecular weight having a marked tendency to assume a crystalline condition, could not be suitably used as the basis for the formation of such substances as flesh and blood.

The greater proportion of the material used by Nature has therefore this colloidal property, and it is only incidentally that definite compounds can be isolated from natural sources which have a crystalline structure. When this is the case, as, for example, in camphor, the compounds lend themselves to treatment by the methods at the disposal of the organic chemist in his laboratory, and it has been found possible, not only to determine their actual structure, that is, the definite arrangement of the constituent atoms in the molecule, but also to prepare them synthetically. The compounds so prepared are in no way different from those occurring in Nature. Many such natural compounds have been so treated, and in many instances, as, for example, in the case of the drug cocaine, the determination of structure has revealed the principle, that is, the particular arrangement of atoms in the molecule, on which the physiological properties of the drug depend. The production of similar laboratory compounds has then

followed, and in many cases the substances so formed have been found more beneficial than the natural material in the exercise of its particular medicinal functions. But the number of these crystalline materials is small compared with the vast number of non-crystalline substances which are utilised by Nature, and little is at present known respecting their use in plant or animal economy. Indeed, the study of these non-crystalline materials and their use in natural processes constitute the sciences of Animal and Vegetable Physiology and of Pathology, the former dealing with the chemistry of the normal processes operating in the living body or plant, and the latter dealing with the corresponding abnormal conditions. These sciences are, however, in reality branches of organic chemistry, although at present our ignorance is such that we are unable to apply our knowledge of structure for their development. Nevertheless, there can be no question that in the not far distant future the whole subject of Biochemistry, which is the chemistry of life, will form but a part of organic chemistry, and we shall be able to apply to it the means and methods which have been attended with such astounding success during the past sixty years in the treatment of the parent science. When this is the case, the causes of our bodily ills will be as clear as the structure of indigo; and their removal as easy as a test-tube reaction. The treatment of disease will be as sure and as certain as the neutralisation of ammonia by sulphuric acid.

But we have still far to go before this stage is reached, for the science of organic chemistry is yet in its infancy, despite the fact that Richter's Lexicon contains the names of some 250,000 definite compounds of carbon with oxygen, hydrogen, and nitrogen, and the activities of research chemists add to these some 3,000 annually. It has been asked sometimes, by people who ought to know better, " What is the use of these laboratory-made compounds, the possible number of which is apparently limitless ? " The answer is supplied by a moment's consideration of the history of the subject and of the ultimate object which it is hoped eventually to attain. The preparation of these large numbers of compounds and their continued production has been, and is, necessary for the determination of structure and for the elucidation of the laws which structure implies.

It is impossible to draw up details of the furniture of a room by taking a photograph of the house in which it is contained, and it is equally impossible to determine the manner in which the atoms of carbon, hydrogen, and oxygen, forming an organic compound, are arranged in the molecule by merely determining the empirical formula of the compound, that is to say, by determining by analysis the relative proportions of the various elements present and expressing the fact by means of an empirical formula, for example, $C_{10}H_{16}O_4$. As a matter of fact, the earlier chemists regarded this as all that was necessary, and the older theories regarding structure were based on this view. Indeed they often applied the methods of the inorganic chemist, and based their proposed synthetical work on the model suggested by inorganic analogy. Thus W. H. Perkin, sen., in 1856, discovered the first coal tar dyestuff, Mauveine, whilst attempting to prepare the alkaloid quinine by a method represented by the empirical equation

$$\underset{\text{(Allyl toluidine)}}{2(C_{10}H_{13}N)}, \text{ that is, } C_{20}H_{26}N_2 + 2O_2 = \underset{\text{(Quinine)}}{C_{20}H_{24}N_2O_3} + H_2O$$

At the present day, no one would attempt such a reaction; not because it is inherently wrong from the arithmetical point of view, but because our present-day knowledge tells us that there are many hundreds of different compounds of the empirical formula $C_{20}H_{24}N_2O_3$ and the likeli-

hood that quinine would be the product in the above reaction is exceedingly remote; also because the structure of quinine is known with a fair degree of certainty and bears no relation whatever to that of allyltoluidine. This stage has been reached through the labours of a large number of research chemists, among whom many of our own countrymen are prominent.

It is evident that if one is to be in a position to determine the structure of complex natural products, some of which contain as many as 1,000 carbon atoms, and thus gain an insight into natural processes, it is necessary to know, in the first instance, the manner in which 2, 3, 4, 5, 6, etc., carbon atoms are capable of joining themselves together and also to know the character and properties of the bodies formed. It must be remembered that there is no royal road in chemical research. Each step has to be made more or less at random, for the investigator is in an unknown country, unmapped and uncharted. There are thus many wrong directions and only one right one, and this has to be found by trial and error based on such knowledge as may have been recorded by previous explorers who have traversed similar regions. The explorer must have, of course, a full knowledge of all previously recorded results, and must base his plans on orthodox lines. Nevertheless, he will often find that the working hypothesis which he has formed after many years of work has led him into a *cul-de-sac* from which he has to extricate himself and start afresh. Still, there are many workers and ultimately the right direction, for a short distance, is ascertained with certainty, and the working hypothesis becomes a theory on which accurate prediction can be based for further work. The labours of the less successful workers are not, however, lost, for they have to be recorded for the use of later pioneers, lest they too go astray. Hence the vast number of substances which have been prepared, investigated, and annotated during the period which has seen the development of organic chemistry to its present state.

In the early days of organic chemical research, that is to say, towards the middle of the last century, it was customary to write the formulæ of organic compounds as if they contained some group (radical) corresponding with the metal in, for example, potassium nitrate,

$C_2H_5NO_3$	KNO_3
Ethyl Nitrate	Potassium Nitrate

but it was soon found that the system was inadequate to express the structure of the radicals themselves. None the less, the theory, although in itself insufficient, led to so much research work in order to verify it that many important discoveries were made, just as the earlier search for the philosopher's stone and the elixir of life led to many surprising and unexpected results in the hands of the alchemists.

The desire to prepare free radicals, that is to say, to isolate ethyl from the above ethyl nitrate in a manner analogous to that by which potassium could be separated from potassium nitrate, enabled Frankland to discover the zinc alkyls, substances which are the prototype of the large number of organo-metallic compounds which, to-day, play so important a part in therapeutics.

The "radical theory" gave place in its turn to the "type theory" by which all organic compounds were relegated to types such as water, ammonia, etc., and here again, after many years' work, research chemists found themselves in a *cul-de-sac*, because organic substances were isolated which could not be relegated to any simple type. To meet this difficulty, more complex types were introduced, but it was evident that chemists were on the wrong lines and that a drastic change in the point of view was essential. Meanwhile, a new system of structural

formulæ was being evolved which reached a high state of development in the hands of Couper. For example, Couper's formula for propyl alcohol—

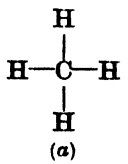
$$\begin{matrix} C\cdot\cdot C\cdot\cdot C\cdot\cdot O\cdot\cdot OH\cdot \\ \dot{H}_3\ \dot{H}_2\ \dot{H}_2 \end{matrix}$$

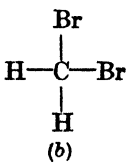
—oxygen being regarded in those days as having the atomic weight 8, is essentially the same as our present formula $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. The extended or graphic system of writing organic formulæ rapidly found favour, but it was evidently insufficient to express many known facts, and it must have occurred to many organic chemists that the one condition lacking, in order adequately to express the structure of carbon compounds, was the projection of graphic formulæ in three dimensions instead of in two dimensions as had hitherto been the custom. It is clear that these views were held by the leading chemists of the time, among whom were Frankland, Odling, and others in this country, as well as the more prominent chemists on the Continent.

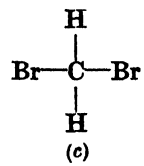
All things in Nature have to be expressed in three dimensions. It is, for example, impossible adequately to draw a picture of a chair or a table unless it is projected in this manner. Merely to draw them in two dimensions, that is, on the plane of the paper, leads to results which are entirely misleading, and can give neither any real idea of the shape of the chair or table, nor, what is more important, can it convey any idea of their positions in relation to surrounding objects. It must be thus with the carbon atom and, without doubt, the greatest impetus given to the new view was the discovery by Pasteur of the relationship between the optically active tartaric acids.

It was, nevertheless, Biot's discovery that the optical activity of tartaric acid persisted in solution which was fundamental, for it showed that the phenomenon was due to the asymmetry of the molecule. The optical activity of soluble inorganic substances does not persist in solution, and in this case the asymmetric structure which produces activity must be due to asymmetric arrangement of the molecules in the crystal, and not to the molecules themselves. The one is therefore due to *intra*molecular, the other to *inter*molecular conditions.

It is unquestionably the influence of Pasteur's work which led van't Hoff and, independently, Le Bel to formulate the tetrahedral theory of the carbon atom, a theory which has led to the development of organic chemistry to a position which places it in the front rank of the exact sciences. Looking backward, it is perhaps remarkable that this theory should have been so long delayed. In 1860 Pasteur likened the two optically active tartaric acids to right- and left-handed screws, and even put forward the suggestion that an explanation for their occurrence could be based on the view that the carbon atom was a tetrahedron, yet it was not until 1875 that van't Hoff's treatise, " La Chimie dans l'espace," was published at Rotterdam. Moreover, it must have been evident to chemists that the formula of the simple hydrocarbon methane could not be expressed on the plane of the paper. To write methane as in (*a*) means that there

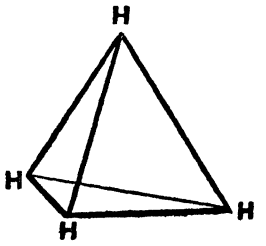

(*a*)


(*b*)

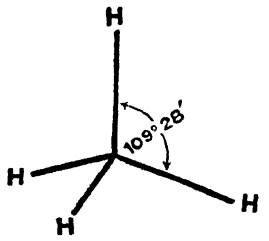

(*c*)

must be two di-derivatives corresponding with the formulæ (*b*) and (*c*), and experiment shows conclusively that when one of the four hydrogen atoms in methane is replaced, the remaining three are still of equal value and that, therefore, the two derivatives (*b*) and (*c*) are the same.

There is only one explanation which can express this, namely, that the four atoms of hydrogen of methane are symmetrically placed about the carbon atom, and the only geometrical figure which conveys this is the regular tetrahedron. It is only by assuming that the four hydrogen atoms are placed at the corners of a regular tetrahedron (*d*) that the properties of methane can be expressed. In other words, the valencies or points of attachment of the hydrogen atoms of methane emerge from the central carbon nucleus in the directions of the axes of a regular tetrahedron, the valencies forming angles of 109°28′ with one another, as in (*e*).

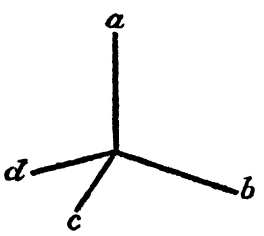


(*d*)

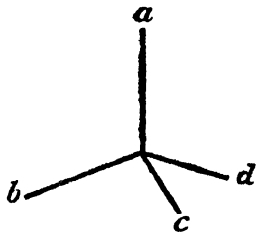


(*e*)

It is evident that the hydrogen atoms in a structure of this kind are all equally placed as regards the carbon nucleus, and that it is immaterial which one is replaced by, say, bromine, the same methyl bromide, CH_3Br, being formed. It is impossible adequately to express the profound influence which this discovery had on the progress of organic chemistry. Points of principle which had remained obscure were rapidly cleared up and new directions for research quickly opened out. The cause of optical activity of the lactic and tartaric acids became evident, for it follows that a carbon atom which is combined with four different groups, *a*, *b*, *c*,



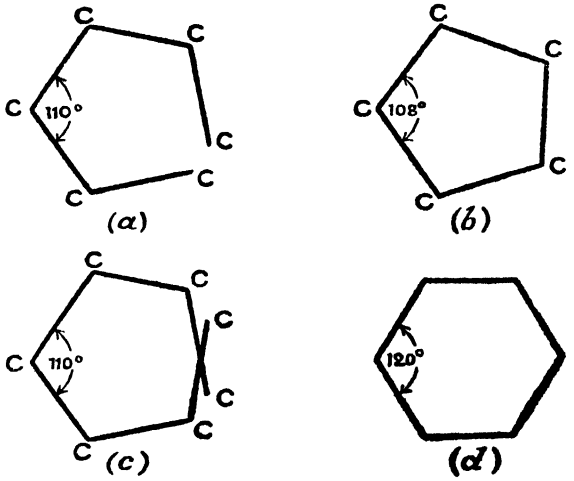
+



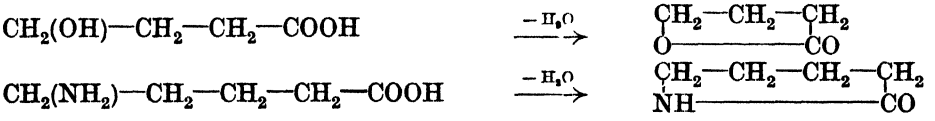
−

and *d*, the so-called " asymmetric " carbon atom, must be capable of yielding two forms which differ from one another in the same manner as our right and left hands, the one being the mirror image of the other. The formulæ, in fact, possess no plane of symmetry, and it is, perhaps, significant that the difference between them should be shown by the rotation of the plane of polarised light to an equal extent in opposite directions. Within more recent years, the discovery has been made by Sir William Pope and his collaborators that several elements other than carbon, for example, tin, can yield optically active asymmetric derivatives, and a similar discovery has been made by Kipping in the case of silicon. Werner has also prepared optically active derivatives of several metals, for example, cobalt and iron.

One of the chief effects of the adoption of the tetrahedral theory of the structure of the carbon atom is shown in the rapid development of synthetic organic chemistry, and perhaps one of the most striking instances of this is illustrated by the work of W. H. Perkin, jun., on the formation and properties of closed carbon rings. If the tetrahedral theory is correct, it is evident that the phrase " a straight chain " of carbon atoms is a misnomer. It has already been mentioned that one of the chief properties of the carbon atom is the capacity it possesses of combining with itself, but this combination cannot form a " straight chain " of carbon atoms as, for example, Couper supposed, because, since the valencies emerge at the tetrahedral angle of 109° 28′, each carbon atom must be joined to the next at this angle. In consequence, as each successive carbon atom is added, the last addition tends to approach more closely to the original carbon atom, until, in the case of a string of five carbon atoms, the two end carbon atoms can be very near together, since the angle of the pentagon is 108°.

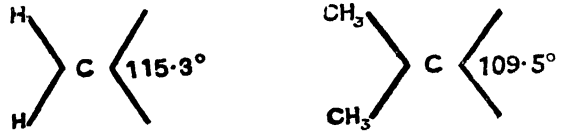


It follows, therefore, that a chain of five carbon atoms (*a*) should be most prone to form a ring or pentagon (*b*) and that a chain of six carbon atoms (*c*) should yield the corresponding hexagon (*d*) with rather greater difficulty, but still with fair ease, since the angle of the hexagon is 120°. Other rings would require a wider deflection of the tetrahedral angle for their production, the deflection being either positive or negative in the sense that for rings up to and including five carbon atoms the tetrahedral angle will have to be diminished to form the ring, and that for rings containing more than five carbon atoms it will have to be increased. Rings other than those containing five or six carbon atoms will require a wider deflection of the tetrahedral angle for their production and, consequently, there will be produced a greater strain and instability in the structures formed. Even before W. H. Perkin carried out his classical researches it was known that 5- and 6-membered rings composed of carbon and other elements such as oxygen and nitrogen were capable of easy formation, and that when, for example, a nitrogen or an oxygen atom occupied the right position in a chain of carbon atoms, that is to say, the third (γ) or fourth (δ) from a carboxyl group (CO_2H) the elements of water were readily eliminated, forming the γ- or δ-lactones or lactams :



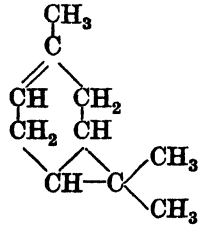
But Perkin, by suitably devised reactions, was able to prepare 3-, 4-, 5-, and 6-membered rings containing only carbon, and was thus able to show that the prediction based on the tetrahedral theory was correct. The general principles involved were summed up by Baeyer in his "strain hypothesis," in which the precise angle through which the carbon tetrahedral angle has to be deflected in order to form the various rings are calculated. Therefrom can be deduced the ease of formation and stability of ring structures generally.

In recent years, the Baeyer strain hypothesis has been materially modified by the work of Thorpe and Ingold, who have proved that the natural angle at which two valencies emerge from a carbon atom, and hence the deflection necessary to produce a given type of ring, is affected by certain factors, notably by the influence of attached groups. It has, for instance, been calculated that whilst the natural inclination of two valencies of a carbon atom carrying two hydrogen atoms is 115·3°, this inclination becomes depressed to 109·5° when the

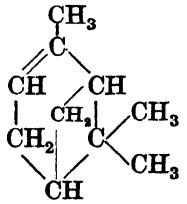


hydrogen atoms are replaced by groups such as methyl, which require a larger share of the space surrounding the carbon nucleus. This attachment of two methyl groups to carbon atoms involved in a 3-, 4-, or 5-membered ring considerably augments the stability of the structure, whilst if the ring contained six or seven carbon atoms a diminution in stability would result.

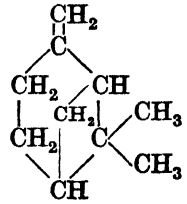
This effect of the twin dimethyl grouping in relieving the strain inherent in small rings is reflected in the structure of many natural products, notably among the essential oils. Many of these compounds, such as carene and α- and β-pinene, have been proved to contain 3- or 4-membered carbon rings, and in every case of this kind one finds, attached to one of the carbon atoms of the small ring, a pair of methyl groups or some equivalent arrangement involving quaternary carbon.



Carene.



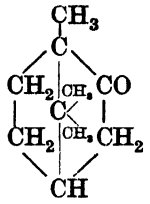
α-Pinene.



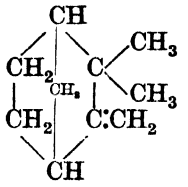
β-Pinene.

In the 5-carbon rings, the strain, although of the same sign, is much smaller, and we find that whilst it is sometimes relieved by the attachment of a twin group, this is not always the

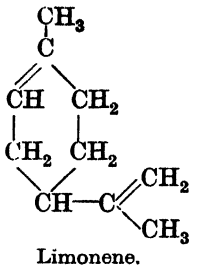
case. Thus in camphor, a twin dimethyl group is found in the one position in which it can function for the molecular comfort of both the 5-carbon rings involved; whilst in camphene only one of the 5-carbon rings is furnished with this grouping, that is, the ring which most requires it owing to the simultaneous presence of the $= CH_2$ group, a destabilising appendage.



Camphor.



Camphene.



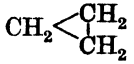
Limonene.

Finally, we notice that in all the naturally occurring 6-membered rings known in terpene chemistry, in which the presence of a twin dimethyl group would augment inherent strain, this group is always absent. In camphor, for example, which has a 6- as well as two 5-membered rings, the twin grouping is situated in the only position in which it can exert no direct influence on the 6-membered ring.

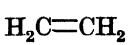
(2) The Unsaturated State

It has already been mentioned that ring formation can be effected even with a chain of three carbon atoms. The three-carbon, or *cyclo*propane ring (I) is, however, difficult to form, and when produced is often unstable.

When the methods used for closing the 3-carbon ring are applied to compounds containing only two carbon atoms, the result is the formation of a double bond between the two carbon atoms, as in formula (II).



*cyclo*Propane.
(I.)



Ethylene.
(II.)

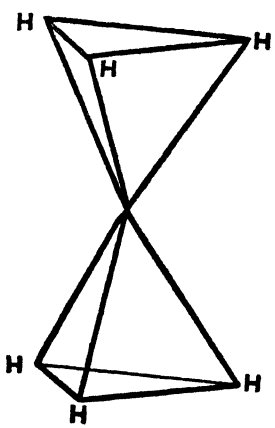


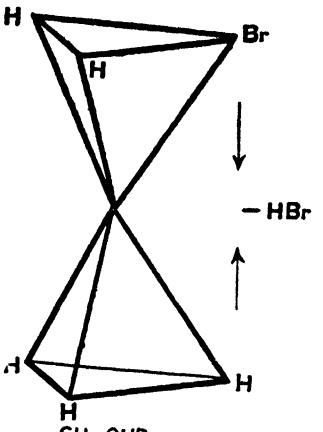
Acetylene.
(III.)

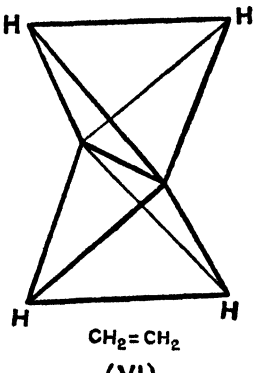
A substance of this kind is known as an unsaturated compound, and it is evident that such a structure can be regarded as the simplest form of ring and one which, in accordance with the strain hypothesis, should be less readily formed and more unstable than the 3-carbon ring. The compounds containing this double linkage are as a matter of fact highly reactive and readily take up hydrogen or other suitable additive element to form derivatives of the fully saturated system. The condition is, therefore, known as the unsaturated state, and is one which has an important bearing on the general structure of carbon compounds. The unsaturated condition can be still further enhanced by the production of a triple linkage between two carbon atoms, as in formula (III), and, in this case, the general properties of the substance are those which might be expected from the formula. Acetylenic compounds are more difficult to produce, and, when produced, are less stable than those based on ethylene. They tend to pass, when treated by suitable reagents, into derivatives of the less unsaturated hydrocarbon and from the present

point of view do not possess any great importance. Excepting in connection with the hydrocarbon benzene, the structure of which will be discussed later, derivatives of this class will not be dealt with further in this narrative.

The possession of an ethylenic unsaturated linkage confers many important properties on an organic compound. It has already been mentioned that two carbon atoms are joined to one another at the points of the two tetrahedra representing them, as, for example, in ethane (IV). The substitution of one of the hydrogen atoms for, say, bromine yields ethyl bromide (V), and the elimination of hydrogen bromide (HBr) from this produces ethylene (VI). It is evident, therefore, that in ethylene the two sides of the two tetrahedra are joined, and not the angular points as in ethane. The outcome is important both from the point of view of stability as well







as from that of reaction, because there can be no doubt that the stability of a carbon compound is dependent on the degree of free motion which is possible within the molecule, and if this free motion is restricted or prevented the stability is lessened or destroyed. It is probable that all things in Nature, from the man on a bicycle to the solar system, depend for their stability on the free motion possible under the prevailing conditions. At any rate, whatever value the argument from analogy may have in this case, it is certain that the stable saturated compounds have the power of free motion about any two carbon atoms contained in them, at the apices of the tetrahedra representing these carbon atoms, and that this free motion is inhibited in unsaturated compounds containing an ethylene or double linkage. This fact can not only be readily understood by an examination of the figures given, but is one which is also fully borne out by experiment.

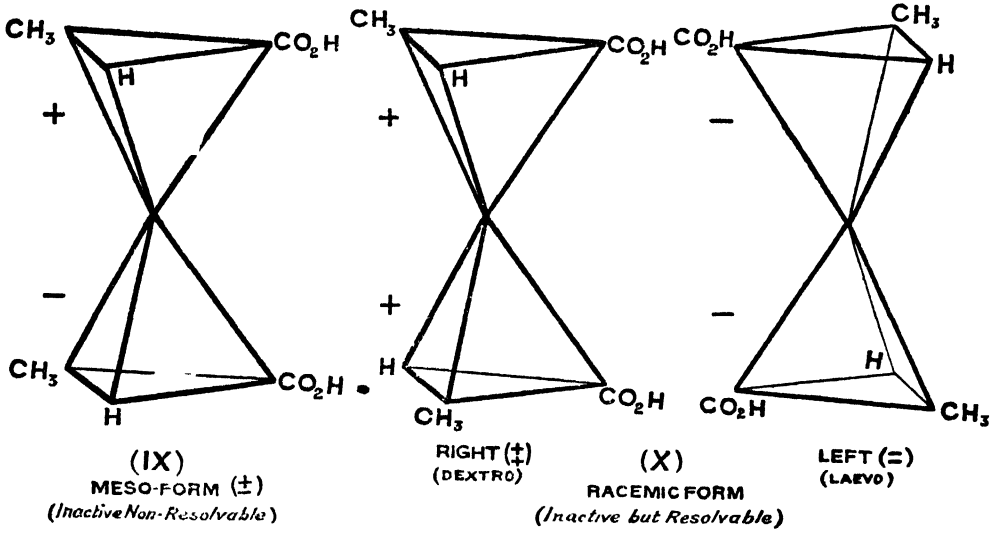
Let us now examine a concrete example, taking, in the first instance, a definite organic substance, say, for example, dimethylsuccinic acid (VII), which we will set up on the tetrahedral models and then predict from them the specific properties and reactions which the substance might be expected to exhibit. We will then examine the actual experimental facts and see how the two agree. Finally, we will do the same with a similar substance in the ethylene series, and we shall then see, not only the astonishing manner in which prediction based on the carbon

tetrahedral theory and experimental verification follow one another, but we shall also be in a position to notice the effect which free rotation in the saturated series and the absence of free rotation in the ethylenic series have on the properties of the compounds concerned.

$$\begin{matrix} CH_3{\cdot}CH{\cdot}COOH \\ CH_3{\cdot}CH{\cdot}COOH \end{matrix}$$
(VII.)

$$\begin{matrix} OH{\cdot}CH{\cdot}COOH \\ OH{\cdot}CH{\cdot}COOH \end{matrix}$$
(VIII.)

It will be noticed that dimethylsuccinic acid (VII) differs from tartaric acid (VIII) in having two methyl groups in place of the two hydroxyl groups. It contains, therefore, two asymmetric carbon atoms, and can, like tartaric acid, exist in two inactive forms, one of which (IX), corresponding with meso-tartaric acid, is built up of a + and a — tetrahedron (see p. 94), and is,



therefore, internally compensated, that is to say, the + effect of the one half neutralises the — effect of the other. It cannot, therefore, be resolved into optically active right and left forms without undergoing molecular fission. The other (X), like racemic acid, is composed of a mixture of two substances each of which has tetrahedra of the same sign, the one having two + tetrahedra and the other two — tetrahedra. The mixture is, therefore, inactive, but is capable of being resolved into its optically active constituents. On the basis of the tetrahedral theory, these forms of dimethylsuccinic acid will appear as in the above diagrams.

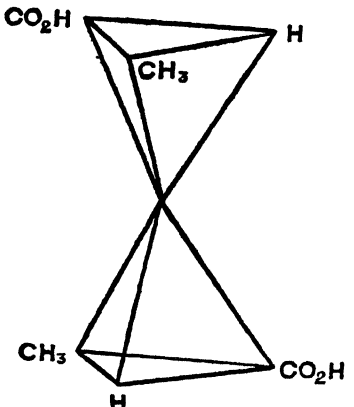
Now it is a rule that like groups, possibly owing to their possession of the same sign of electrical charge, repel one another, consequently the most stable form of the meso-acid—free rotation being assumed—will be (XI) in which it will be noticed that all three like groups are as remote from one another as possible and, therefore, the greatest molecular comfort, that is, stability, possible in the circumstances is attained. On the other hand, the racemic form will be most stable as shown (X), because it is not possible, in the case of either constituent, to rotate the tetrahedra so as not to leave two similar groups in contiguous positions. It follows, therefore, that this racemic form will be less stable than the meso-modification.

We are now, therefore, in a position to make the following predictions:

(*a*) Dimethylsuccinic acid will exist in two inactive forms, one incapable of being resolved into optically active constituents, the other yielding right- and left-handed optical forms under suitable treatment.

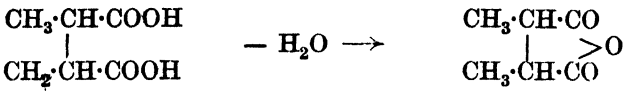
(*b*) The form which is not capable of being resolved into optically active constituents will be definitely more stable than the acid which can be so resolved; in other words, the resolvable acid will be readily convertible into the non-resolvable acid, but not *vice-versâ*.

We can, moreover, make further predictions respecting the reactions of these acids by carefully studying the tetrahedral models. It has been mentioned already, for example, that



(XI)
STABLE POSITION OF MESO-FORM

there exists among carbon compounds and also among compounds containing carbon and oxygen a marked tendency to form a 5-membered ring when conditions are present which conduce to such a change. These conditions are, as a matter of fact, present in dimethylsuccinic acid, because it is possible for the two carboxyl groups (COOH), under suitable treatment, to eliminate the elements of water and to pass into the anhydride (XII). It is evident that, in order that

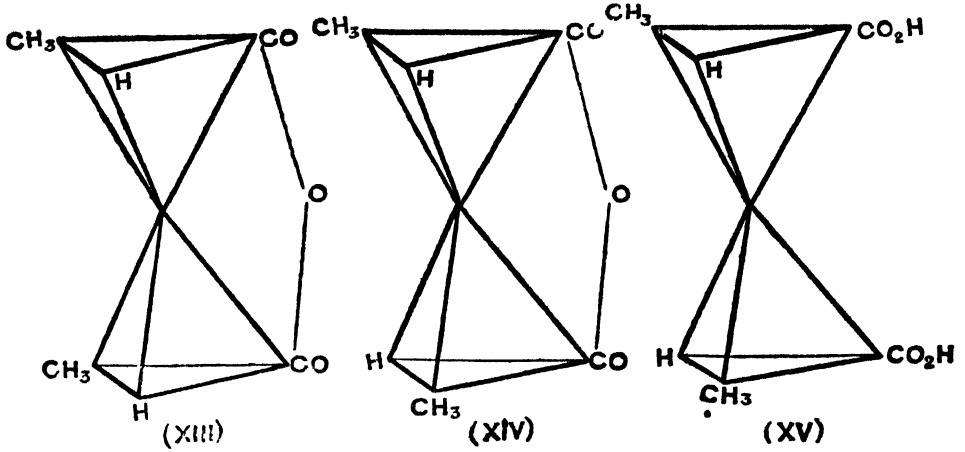


Anhydride
(XII)

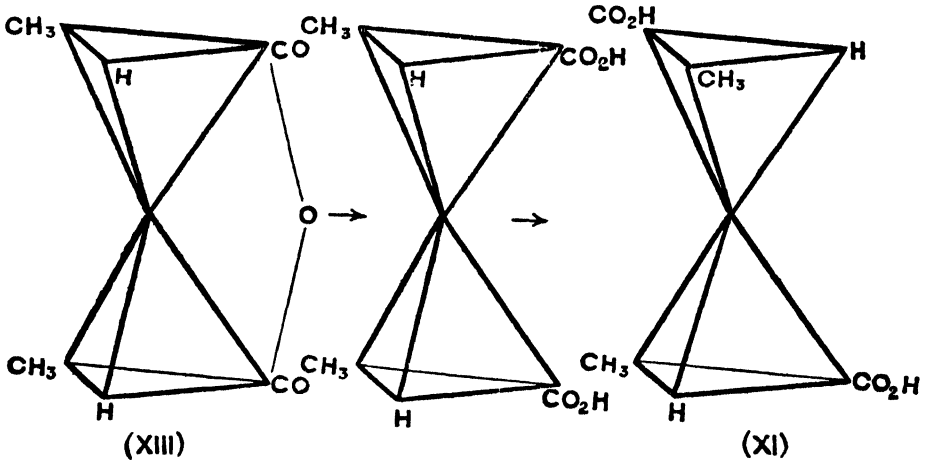
the meso-acid may do this, it is necessary that free rotation should first occur so as to bring the two carboxyl groups on the same sides of the tetrahedrons as in (IX). The anhydride is then formed yielding the structure (XIII).

But anhydride formation of this kind again brings like groups into adjacent positions; consequently, it is to be expected that the condition will be an unstable one and will change under suitable treatment into a form in which these groups are as remote as possible, as in (XIV).

This change involves the movement of two units, of which one is a hydrogen atom; in fact, it means an interchange in the positions of the methyl group and the hydrogen atom. We do not yet know in what manner this change occurs. What we do know is that it is a phenomenon



of very frequent occurrence among compounds of carbon, and is always resorted to when, by doing so, the substance can attain greater molecular stability. In some optically active compounds, the formation of a derivative leads to a complete reversal of sign—a phenomenon which is known as the "Walden inversion"; in others under similar conditions, "racemisation,"



or the production of an "inactive compound," occurs. These are phenomena which are produced by the same kind of change as that mentioned above.

Anhydrides are substances which readily react with water, forming the open-chain acid.

Thus, it is to be expected that the anhydride of the meso-form (XIII) will revert to the meso-acid (XI) on treatment in this manner :

$$\begin{matrix}CH_3\cdot CH\cdot CO\\ CH_3\cdot CH\cdot CO\end{matrix}\!\!>\!O \;+\; H_2O \;\longrightarrow\; \begin{matrix}CH_2\cdot CH\cdot COOH\\ CH_3\cdot CH\cdot COOH\end{matrix}.$$

On the other hand, the hydration of the stable form of the anhydride (XIV) will lead to the formation of the structure (XV), which, it will be noticed, is one of the individuals contained in the racemic form. It might be thought that the substance so produced would therefore be an optically active form, but it appears to be a general law that synthesis from inactive materials always leads to inactive products, consequently, although possibly in the above reaction the optically active member is produced momentarily, it at once becomes inactive owing to the formation of an equal quantity of its enantiomorph. The acid formed by the hydration of the stable anhydride will therefore be the racemic form, and our further predictions are as follows :

(*c*) Each acid will yield an anhydride. That from the stable non-resolvable acid will be definitely less stable than that from the less stable (labile) resolvable acid and will be capable of conversion into it under suitable conditions. The reverse change will not be found possible.
(*d*) Each anhydride will yield its own acid on hydration.

The experimental facts are these :

(*a*) Dimethylsuccinic acid can be isolated in two forms, one melting at 192–194° and the other at 120–123°. The lower melting acid can be resolved into dextro- and lævo-forms, and is definitely less stable than the higher melting acid, since it is completely converted into it on treatment with hydrochloric acid at 190°.
(*b*) Each acid gives an anhydride. That from the acid melting at 192–194° melts at 38°, that from the acid melting at 120–123°, at 87°. The anhydrides yield their respective acids on hydration.
(*c*) The anhydride melting at 38° is definitely less stable than the anhydride melting at 87°, since it is completely converted into it on distillation.
(*d*) The direct change from the higher melting acid to the lower melting one, or from the higher melting anhydride to the lower, is not apparently possible.

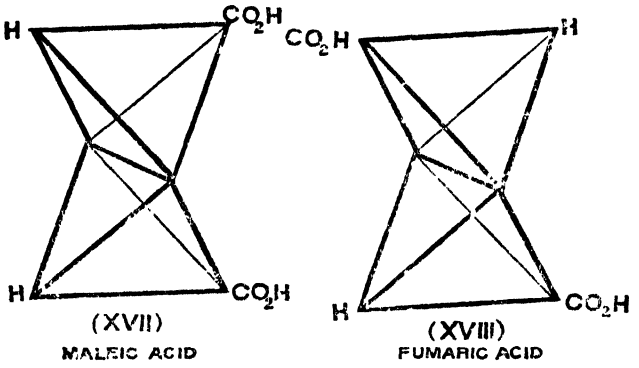
It should be added that the possession of a higher melting point is nearly always associated with stability, and that the occurrence of forms such as those described above is always a property of the type illustrated. At the present time, it is usual to call the higher melting, stable acid the *trans*-form, and the less stable acid, the *cis*-modification.

We can now take a similar acid in the ethylene series and show how the absence of free rotation affects the reactions of the substance, but in this instance it is sufficient to take, as an example, the simplest member of the series, namely, the acid of formula (XVI).

When this compound is set up on the tetrahedral models it will be seen at once that there will be two distinct forms, namely, (XVII) and (XVIII). One of these, that is, the acid of formula (XVII), will readily yield an anhydride, because the two carboxyl groups (COOH) are

on the same sides of the figure and close together. On hydration, this anhydride should yield the same acid as that from which it was derived. The second acid (XVIII) will give no anhydride, because the two carboxyl groups are now placed on opposite sides of the figure, and the absence of any possibility of free rotation prevents them from being brought closer together. Moreover, since the first acid (XVII) has like groups on the same sides of the figure, it will be definitely less stable than the second acid (XVIII), in which like groups are as remote as possible, thus it is

CH·COOH
||
CH·COOH
(XVI.)

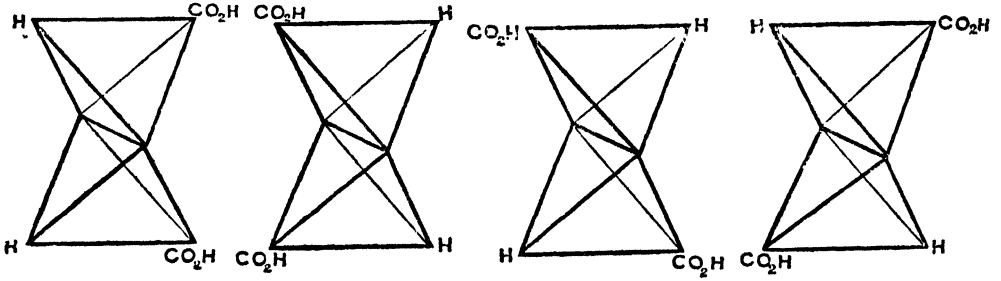


(XVII)
MALEIC ACID

(XVIII)
FUMARIC ACID

to be expected that the first acid (XVII) will be convertible into the second under suitable conditions.

Again, each acid contains a plane of symmetry and, therefore, neither of them will be capable of resolution into optically active forms. If any doubt exists on this point, it can be set at rest by building up the mirror image of each acid. If the mirror images are superimposable on the objects, planes of symmetry must be present, and, consequently, no resolution can be effected. It is clear that the mirror image (*b*) and the object (*a*) are superimposable if either be turned



(*a*) (*b*) (*c*) (*d*)

through an angle of 180°, and that, in like manner, the mirror image (*d*) and the object (*c*) are also superimposable. The predictions from the models can then be summarised as follows :

(*a*) An acid of formula (XVI) will exist in two forms, one of which will give an anhydride and the other will not. The acid yielding an anhydride will be less stable than the acid from which no anhydride can be formed.

(*b*) Neither acid will be capable of resolution into optically active forms.

The facts are as follows :

(*a*) The acid of formula (XVI) can be isolated in two modifications, fumaric acid which sublimes at 200° and maleic acid which melts at 135°.

(*b*) Maleic acid yields an anhydride melting at 53° which is reconverted into maleic acid on hydration. Maleic acid is definitely less stable than fumaric acid, and is converted into it on treatment with hydrochloric acid in a sealed tube. Fumaric acid does not yield an anhydride.

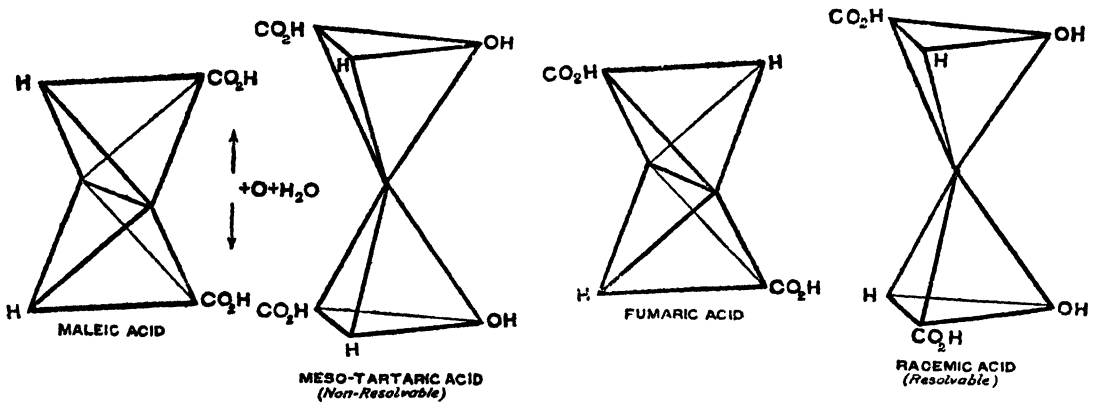
(*c*) Neither maleic nor fumaric acids can be resolved into optically active forms.

The experimental facts are, therefore, in complete accordance with the predictions.

Finally, it is possible to apply a confirmatory experimental proof that the conclusions set out above are correct, because, if they are, it follows that, since maleic and fumaric acids are ethylenic acids, they should be readily convertible into the corresponding saturated acids on suitable treatment. It should be possible, therefore, to break the double linkage by means of a suitable oxidising agent, in accordance with the general equation :

$$\begin{matrix} CH\cdot COOH \\ \| \\ CH\cdot COOH \end{matrix} + O + H_2O \longrightarrow \begin{matrix} (HO)\cdot CH\cdot COOH \\ | \\ (HO)\cdot CH\cdot COOH \end{matrix}$$

—in other words, to re-form the tartaric acids from both fumaric and maleic acids, a change which, if the theory is correct, should be represented by the following scheme :



This has been effected experimentally. Maleic acid gives, on oxidation, the internally compensated, non-resolvable, meso-tartaric acid, whereas fumaric acid on similar treatment gives the externally compensated, resolvable racemic acid. The above instances of prediction from theory and verification by experiment illustrate, in a remarkable degree, the fact that deductive reasoning, based on the tetrahedral models of the molecules of carbon compounds, renders it possible to predict, not only the occurrence, but also the properties of such compounds.

The conversion of compounds containing ethylenic linkages into saturated compounds by the addition of hydrogen finds an important industrial application in the formation of saturated fats from those having an unsaturated structure. The natural fats are usually glycerides, that

is to say, they are ethereal salts of the higher fatty acids with the alcohol glycerine. The formula of the typical animal fat, stearin, is given in (XIX) and its commercial importance lies in the

$$\begin{array}{l}CH_2O\cdot OC\cdot C_{17}H_{35}\\ CHO\cdot OC\cdot C_{17}H_{35}\\ CH_2O\cdot OC\cdot C_{17}H_{35}\end{array} + \begin{array}{c}3H_2O\\ \text{or}\\ 3NaOH\end{array} \rightarrow \begin{array}{l}CH_2\cdot OH\\ CH\cdot OH\\ CH_2\cdot OH\end{array} + \begin{array}{c}3C_{17}H_{35}\cdot COOH\\ \text{or}\\ 3C_{17}H_{35}\cdot COONa\end{array}$$

Stearin. (XIX.) — Glycerine. — Stearic acid or sodium stearate.

fact that on hydrolysis (action of water or caustic alkali) it yields glycerine and sodium stearate, the latter being the basis of hard soap. Stearic acid, which is itself used as a constituent of paraffin candles, has a structure represented by the formula (XX), and contains an unbranched chain of carbon atoms as in (XXI).

$$CH_3—(CH_2)_{16}—COOH \qquad (XX.)$$

$$CH_3—CH_2—CH_2—CH_2—CH_2—COOH \qquad (XXI.)$$

It happens that many fats and oils, usually of vegetable origin, have a structure very similar to that of stearin, only instead of being based on a saturated substance like stearic acid, they are glycerine esters of the corresponding ethylenic compound—oleic acid. As is to be expected, these ethereal salts (olein, XXII), behave in the same manner as stearin :

$$\begin{array}{l}CH_2O\cdot OC\cdot C_{17}H_{33}\\ CHO\cdot OC\cdot C_{17}H_{33}\\ CH_2O\cdot OC\cdot C_{17}H_{33}\end{array} + \begin{array}{c}3H_2O\\ \text{or}\\ 3NaOH\end{array} \rightarrow \begin{array}{l}CH_2\cdot OH\\ CH\cdot OH\\ CH_2\cdot OH\end{array} + \begin{array}{c}3C_{17}H_{33}\cdot COOH\\ (XXIV.)\\ \text{or}\\ 3C_{17}H_{33}COONa\\ (XXIII.)\end{array}$$

Olein. (XXII.) — Glycerine. — Oleic acid or sodium oleate.

but the sodium oleate (XXIII) produced is not suitable for use as hard soap, and oleic acid (XXIV) is a liquid. Consequently, the conversion of the unsaturated fat into the saturated fat on the commercial scale became a matter of considerable importance.

The structure of oleic acid is known : it is (XXV), the ethylenic linkage being exactly in

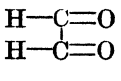
$$\underset{\text{Oleic acid (XXV.)}}{CH_3\cdot(CH_2)_7\cdot CH{=}CH(CH_2)_7\cdot COOH} + H_2 \rightarrow \underset{\text{Stearic acid.}}{CH_3\cdot(CH_2)_7\cdot CH_2—CH_2(CH_2)_7\cdot COOH}$$

the middle of the unbranched chain of carbon atoms; moreover, its relationship with stearic acid as shown by the above equation was also known. The discovery that this change could be effected by gaseous hydrogen in the presence of a catalyst, for example, nickel, supplied a commercial process, known as the oil-hardening process, which is used at the present time for the production of enormous quantities of saturated fats.

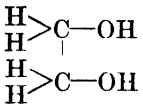
The Occurrence of Colour.—One of the chief phenomena associated with the double or ethylenic linkage is the occurrence of colour in certain compounds in which it is contained. In

the first place, it is, perhaps, desirable to define colour as it is understood by the organic chemist, because the possession and origin of colour are matters of very considerable importance from many points of view, and, later on, in connection with the chemistry of benzene, will be found to form the basis of that large and technically important group—the so-called coal-tar dyestuffs.

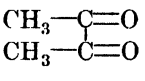
The production of visible colour is due to the fact that the compound possessing colour has the property of causing selective absorption in the visible region of the spectrum. If the absorption occurs in the red region of the spectrum, the substance will be blue; if in the blue region, it will be red. There are, however, wide regions of the spectrum which are not visible to the eye and can only be detected and investigated by means of the photographic plate. These regions are called the infra-red and the ultra-violet, and organic substances which have the power of causing absorption in these regions must be regarded as coloured, although to the eye they appear colourless. A true colourless substance is one which produces general absorption throughout the whole accessible region of the spectrum, and it is to this class that the greater number of organic compounds belong. Indeed, all saturated compounds, and most of those which are unsaturated, are of this type. There are, however, a certain number of unsaturated compounds which possess visible colour, and these are all associated with a structure containing a system of alternating double and single linkages. Such a structure may, apparently, be held by a compound composed of carbon atoms alone, or by one which contains carbon atoms together with oxygen or nitrogen atoms. In fact, any element can be used in this connection which has the power of coupling itself by two valencies with carbon. The simplest possible compound containing a system of this kind is glyoxal (XXVI), in which it will be seen that there



(XXVI.)



(XXVIII.)



(XXVII.)

are two double linkages separated by one single linkage. This compound is a yellow solid at low temperatures and a yellow gas in ordinary circumstances. Diacetyl (XXVII) is a yellow liquid at room temperature.

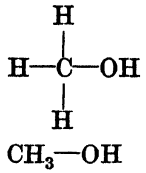
That the colour of these compounds is an outcome of their structure is shown by the fact that when the structure is destroyed, that is to say, when the ethylenic linkages are removed by the addition of hydrogen, the colour vanishes. Thus the substance glycol (XXVIII) is colourless.

(3) The Functions of Oxygen and Nitrogen

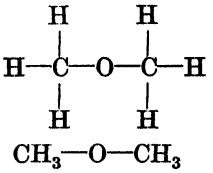
Oxygen.—Oxygen is one of the chief elements which enters into the structure of organic compounds and functions, usually, in its divalent form.

In this condition, it may have one valency combined with carbon and the other with hydrogen, in which case the alcohols, for example, methyl alcohol (XXIX), are produced, or, it may have its two valencies coupled with two different carbon atoms, as in the ethers, for example, dimethyl ether (XXX), or, again, both valencies may be united with the same carbon atom, and in this

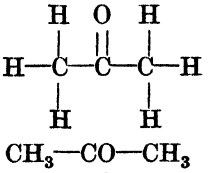
case the ketones, for example, dimethyl ketone (acetone) (XXXI), or the aldehydes, for example, acetaldehyde (XXXII), are the products formed :



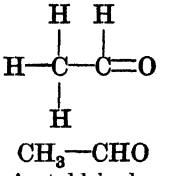
$CH_3—OH$
Methyl alcohol.
(XXIX.)



$CH_3—O—CH_3$
Dimethyl ether.
(XXX.)

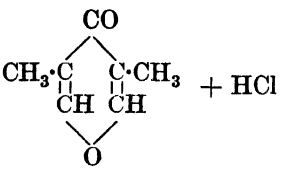


$CH_3—CO—CH_3$
Dimethyl ketone.
(XXXI.)

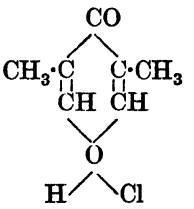


$CH_3—CHO$
Acetaldehyde.
(XXXII.)

It can, moreover, also function in the tetravalent state, a fact which was first clearly shown by Collie, who prepared dimethylpyrone (XXXIII) and showed that it formed a salt with hydrochloric acid (XXXIV) :



(XXXIII.)



(XXXIV.)

There can be little doubt that many flowers owe their colour to the formation of salts of this kind; this will, however, be dealt with more fully elsewhere in this volume. As a general rule, compounds containing oxygen combined with two atoms of carbon, such as the ethers, possess little general interest; those, however, which have one of the oxygen valencies joined with carbon and the other with hydrogen, that is, the alcohols, are of considerable importance.

The Alcohols.—The lowest member is methyl alcohol, $CH_3{\cdot}OH$, which is one of the products formed by the distillation of wood. It will be referred to later in connection with the preparation of formaldehyde. The most important member is, however, ethyl alcohol, $CH_3–CH_2–OH$, which is of particular interest, because it is one of the substances which is produced by the action of certain compounds called enzymes on several sugars and higher carbohydrates such as starch and cellulose. The enzyme is an organic substance of high complexity, it is non-living and, therefore, works chemically or physically, but the actual manner in which it accomplishes its task is not known. Its function in the plant is to set free the store of energy which has been accumulated in the form of the sugars and sugar-like constituents, each variety of plant having, apparently, its own particular enzyme, which can only operate on the material of that plant. The formation of alcohol from a sugar, for example, glucose, cannot be carried out in the laboratory by known reactions, although the process by which the enzyme breaks down the molecule of starch into glucose can be reproduced by mineral acids. A full account of these matters will be found in another chapter. It is evident that the discovery of a suitable agency for the production of alcohol from waste products is a matter of very considerable importance in connection with the economic production of motor fuel. Starchy materials, cereals, etc., can readily be converted into alcohol, but starch is the basis of our staple foods, and already the problems of the world's food supplies cause anxiety. Pure cellulose can also

be converted into glucose and hence into alcohol quite easily, but the behaviour of cellulose in its various forms is not yet clearly understood, and the problem of the economic production of alcohol from the cellulose of, for example, wood fibre still remains unsolved. It is evident that, locally, large quantities of alcohol can be manufactured from sugar residues such as molasses, and this is, as a matter of fact, done. But the quantity produced in this way is small compared with the enormous annual consumption of motor fuel, and it will be noticed that in this case also material is used which would otherwise be employed as cattle fodder.

It is possible to produce higher alcohols by the enzymatic disruption of the ponderous molecules which constitute the starches and, consequently, amyl alcohol, C_5H_{11}–OH (fusel oil), is usually present in the alcohol produced by fermentation. The next lower member, butyl alcohol, CH_3–CH_2–CH_2–CH_2–OH, seemed likely, at one time, to acquire considerable technical importance owing to the fact that the unsaturated hydrocarbon, butadiene, CH_2=CH—CH=CH_2, which can be formed from it, has the property of polymerising (setting) to a rubber-like substance under suitable conditions. True rubber, that is, natural rubber, is, as Tilden showed, based on isoprene, CH_2=CH—C(CH_3)=CH_2, the unsaturated hydrocarbon next higher in the series to butadiene, which can not only be formed from rubber, but also passes back into it on polymerisation. The commercial production of isoprene is, however, too difficult and costly, and, if the rubber formed from butadiene had proved satisfactory, there is no doubt that its commercial production from butyl alcohol would have been feasible, because it is possible, by the suitable fermentation of starch (rice, for example) to prepare large quantities of butyl alcohol. It is true that the butyl alcohol obtained in this way is accompanied by a proportionate amount of acetone, CH_3–CO–CH_3, but, as this substance always finds a ready market, the success of the process would have been assured. Unfortunately, butadiene rubber has never entered into serious competition with the natural product, and the problem of the economic synthesis of rubber is still unsolved.

Another higher alcohol which can be made by fermentation is glycerine, CH_2(OH)–CH(OH)–CH_2(OH), a substance which has already been mentioned in connection with the hydrolysis of fats. The compound is of great interest from the fact that it is the basis of the explosive nitroglycerine, a constituent of cordite and of most of the safety blasting agents permitted by the Home Office for use in mines. Although there will be a section devoted to explosives in this book, it is perhaps of interest, in passing, to notice the peculiar characteristics of nitroglycerine, which may be regarded as a typical organic explosive. Before the discovery of this substance, the only explosives were those which contained two or more components, such as, for example, the mixture of potassium nitrate, sulphur and charcoal known as gunpowder. The explosion of these mixtures was merely combustion carried out very rapidly. It was, in fact, intermolecular in character, that is to say, molecules of two chemical substances reacted to bring about the explosion. The explosion of an organic explosive is, on the other hand, intramolecular in character, that is to say, it is brought about by the disruption of the organic molecule itself, a process which, in the case of nitroglycerine, can be represented thus :

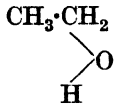
$$2\ \begin{matrix} CH_2\cdot O\cdot NO_2 \\ | \\ CHO\cdot NO_2 \\ | \\ CH_2O\cdot NO_2 \end{matrix} \longrightarrow 6CO_2 + 5H_2O + 2N_2 + N_2O.$$

Nitroglycerine.

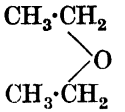
The explosion can therefore be initiated by shock, which can be imparted either by a blow

or by the impulse given by the detonation of some other explosive, for example, mercury fulminate.

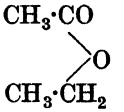
Ethereal Salts and Ethers.—It is often convenient when dealing with the nomenclature of groups to revert to the type theory and to illustrate structure by means of a name based on this system. For example, it is convenient to regard alcohols as compounds based on the water type in which a hydrocarbon radical (C_2H_5) replaces hydrogen as in ethyl alcohol (XXXV). In the same way, the ethers are compounds of type (XXXVI) and the ethereal salts are compounds in which the hydrogen atoms of water are respectively replaced by an acid radical (CH_3–CO) and a hydrocarbon radical (C_2H_5) (XXXVII):



Ethyl alcohol.
(XXXV.)



Diethyl ether.
(XXXVI.)



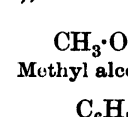
Ethyl acetate.
(XXXVII.)

The ethereal salts are characterised by the ease with which they react with water, especially in the presence of mineral acids, undergoing disruption (hydrolysis) into the corresponding alcohols and acids:

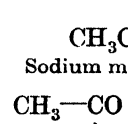
$$\underset{\text{Ethyl acetate.}}{CH_3—COO\cdot C_2H_5} + H_2O \rightarrow \underset{\text{Acetic acid.}}{CH_3—COOH} + \underset{\text{Ethyl alcohol.}}{C_2H_5\cdot OH}$$

The Acids.—The presence of a hydroxyl group (OH) is the cause of the conference of acid properties on an organic substance, just as the presence of an amino-group (NH_2) is usually the cause of the occurrence of basic properties; but the degree of basicity or acidity is markedly affected by the character of the other groups attached to the carbon atom with which the hydroxyl or amino-residues are combined.

In the alcohols and primary amines (–NH_2), the lowest degree of acidity and the highest degree of basicity is reached in the mono-substitution series, because the alkyl group, which is electro-positive in character, enhances, in the one case, the electro-positive character of the nitrogen, and, in the other, diminishes the electro-negative function of the oxygen. The alcohols are thus only feebly acid and form salts which are readily dissociated by water. When, however, a hydrocarbon radical is present which exerts an electro-negative influence, such as, for example, the phenyl group (C_6H_5), the alcohol, for example, phenol or carbolic acid (XXXVIII), is a markedly acid substance:



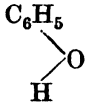
Methyl alcohol.



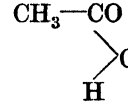
Sodium methylate.



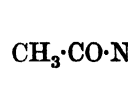
Methylamine.



Phenol.
(XXXVIII.)



Acetic acid.
(XXXIX.)

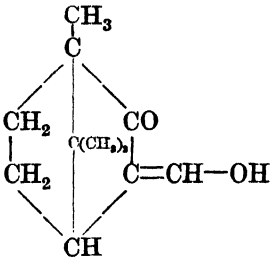


Acetamide.
(XL.)

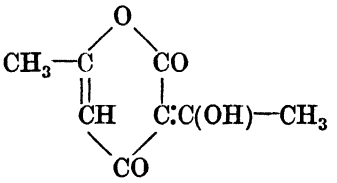
It follows, therefore, that a strongly electro-negative acid radical, for example, acetyl (CH_3–CO–) will exert a distinct electro-negative effect on the system, and that a substance like

(XXXIX) (acetic acid) will be strongly acid in character. It follows, also, that the effect of the acid radical will be diminished by its attachment to nitrogen, and that a substance like acetamide (XL) will be only feebly basic in character.

It is usual, then, to regard the group O=C—OH, or the carboxyl group, as the chief acid-forming group, and, as a matter of fact, the large majority of organic acids contain this group. It must be remembered, however, that acidity is, as already stated, a function of the hydroxyl group, and is increased or diminished in accordance with the electropolarity of the molecule to which it is attached. Thus hydroxymethylenecamphor (XLI) is a strongly acid substance and dehydracetic acid (XLII) has acid properties stronger than those of acetic acid (XXXIX), although the two first-named compounds contain no carboxyl group.



Hydroxymethylene camphor.
(XLI.)

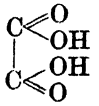


Dehydracetic acid.
(XLII.)

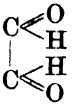
$CH_3 \cdot COOH$

Acetic acid.
(XXXIX.)

There are, however, certain indications which render it doubtful if the formula O=C—OH adequately represents the actual structure of this group. Several considerations, such as, for example, the absence of colour in oxalic acid (XLIII), which should be coloured, like glyoxal (XXVI), and the fact that carboxylic acids do not usually give reactions indicative of the



Oxalic acid.
(XLIII.)



Glyoxal.
(XXVI.)

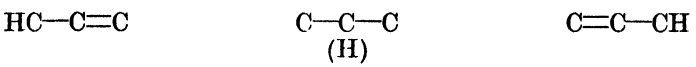
carbonyl group (C=O), seem to suggest that some other arrangement of the atoms is more likely to be correct. In the next section, in which the problem of tautomerism is dealt with, it is pointed out that in all systems composed of three elements, either the same or different, which contain two singly- and two doubly-bound atoms, and in which a hydrogen atom is attached to the terminal singly-bound element, there is always a tendency for that hydrogen atom to take up its position on the other terminal element of the system with a consequent shifting of the double bond, thus :

$$HC—C=O \quad \rightleftharpoons \quad C=C—OH.$$

Such a change is known under the name of a " tautomeric change," and is of frequent occurrence among organic compounds. It is obvious, however, that any change of this kind, when applied to the carboxyl group, does not lead to any change of structure; it merely postulates the existence of a mobile hydrogen atom in the system :

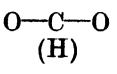
$$O=C—OH \quad \rightleftharpoons \quad HO—C=O.$$

Nevertheless, it has been shown that in a symmetrical tautomeric system, in which the two terminal elements are the same, as is the case with the carboxyl group, and, also, for example, in the three-carbon system, there is a tendency for the mobile hydrogen atom to take up a position on the central atom of the system, and that the compounds so produced have a considerable measure of stability—they are, in fact, semi-aromatic in character, an expression which will be more clearly understood when the section on the chemistry of benzene has been



Three carbon system.

read. On this hypothesis, the formula of the carboxyl group will become either (XLIV) or more likely (XLV), and a formula of this kind would account for many of the peculiar properties of compounds containing this group.



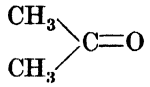
(XLIV.)



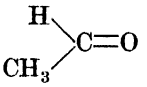
(XLV.)

The Ketones and Aldehydes.—These substances contain oxygen which has both of its valencies joined to the same carbon atom. Since they contain two doubly-linked elements, they must be regarded as unsaturated compounds and, as a matter of fact, all their reactions conform to this point of view.

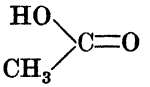
In the ketones, the two remaining valencies of the carbon atom, that is, those not satisfied by the divalent oxygen, are coupled with two other carbon atoms, but in the aldehydes only one of these valencies is so coupled, the other being attached to hydrogen. The aldehydes are therefore more reactive than the ketones, and tend readily to pass, on oxidation, into the corresponding acids—*e.g.* acetaldehyde (XLVI) into acetic acid (XXXIX).



A ketone (acetone).

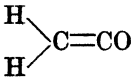


An aldehyde (acetaldehyde).
(XLVI.)

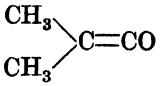


Acetic acid.
(XXXIX.)

It is possible to prepare compounds in which both the remaining valencies of the carbon atom coupled with oxygen are attached to the same carbon atom, for example, in keten (XLVII) and dimethylketen (XLVIII):



(XLVII.)

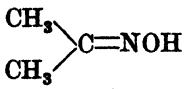


(XLVIII.)

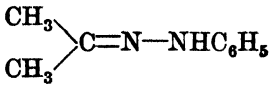
But, as is to be expected, substances of this type are not only very difficult to prepare, but, as they represent a high degree of unsaturation, they are extremely reactive.

The reactions of the aldehydes and ketones are very similar and the presence in them of the carbonyl group (C=O) can usually be detected readily by the so-called ketone reagents, hydroxylamine, $H_2N—OH$, phenylhydrazine, $H_2N—NH—C_6H_5$, and semicarbazide,

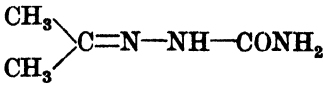
$H_2N—NH—CO—NH_2$. In each case, the two hydrogen atoms, written first in the formulæ, form water with the carbonyl oxygen of the ketone or aldehyde, giving, usually, well-defined crystalline compounds of the type shown below:



Acetoxime.



Acetone phenylhydrazone



Acetone semicarbazone.

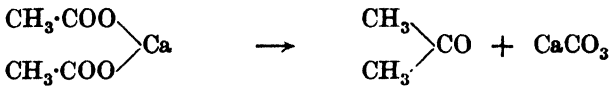
The ketones and aldehydes are often important substances in perfumery. The simplest aldehyde, formaldehyde, H—CHO or $\begin{matrix}H\\H\end{matrix}\!\!>\!C=O$, is a powerful and valuable disinfectant and bactericide; it is used in very considerable quantities for these purposes, for example, in the freeing of raw wool from anthrax bacteria. The production of formaldehyde is therefore an important problem, which is not entirely solved by its present mode of production by the oxidation of methyl alcohol. All methyl alcohol has to be obtained by the distillation of wood, and its separation from the distillate is a comparatively costly operation; moreover, wood distillation is not carried out extensively in this country.

So far, all attempts which have been made to prepare the aldehyde by the interaction of carbon monoxide and hydrogen thus:

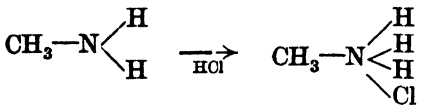
$$CO + H_2 \longrightarrow HCHO$$

have proved ineffective, owing to the fact that the right catalyst has not yet been discovered.

The simplest ketone, acetone, $CH_3—CO—CH_3$, has already been mentioned as being one of the products accompanying butyl alcohol in the fermentation of starch. Like methyl alcohol, its usual source of origin is the wood distillate which contains acetic acid, and from this acetone is prepared by the distillation of the calcium salt:

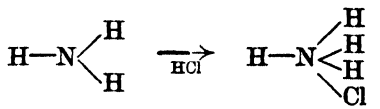


Nitrogen.—Nitrogen may function either as a trivalent or pentavalent element in an organic compound; in the trivalent condition, it is in its basic form and passes into the pentavalent state when these bases form salts. The analogy, therefore, with the type ammonia is complete:



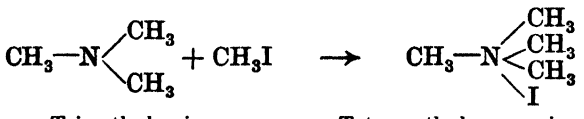
Methylamine.

Methylamine hydrochloride.



Ammonia.

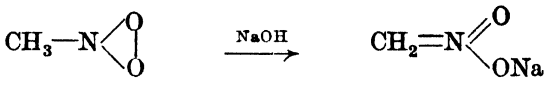
Ammonium chloride.



Trimethylamine (tertiary).

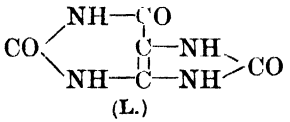
Tetramethyl ammonium iodide (quaternary).

It also passes into the pentavalent condition when tertiary bases pass into quaternary salts as shown above. It appears to be the rule that organic nitrogen compounds containing the element in the trivalent form are definitely more stable than those which have it in the pentavalent condition, and that the latter tend to pass into the former on suitable treatment. It seems, at first sight, that the nitro-compounds, $CH_3—NO_2$, are exceptions to this rule; but it is possible that these substances, for example, nitro-methane, have the formula (XLIX), and that their transformation into the salt is accompanied by a change from the trivalent to the pentavalent state:

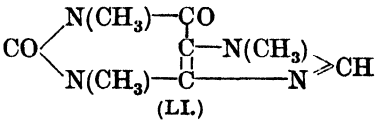


(XLIX.) Sodium salt.

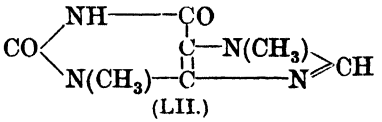
Nitrogen plays an important part in the structure of many organic substances utilised by Nature in animal and vegetable economy. In the animal kingdom, one of the chief products is urea, carbamide, $NH_2—CO—NH_2$ (to which Werner assigns the ring structure $C(OH)\langle{}^{N}_{NH_2}\rangle$), a substance which may be regarded as one of the ultimate products of animal metabolism from the complex proteins. An intermediate compound is uric acid (L), the structure of which has been determined, and closely related with it are the products of vegetable change, caffeine (LI) and theobromine (LII), the former being the essential principle of coffee and tea and the latter of cocoa. All these substances have been prepared synthetically in the laboratory.



(L.)

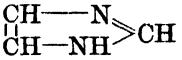


(LI.)



(LII.)

Many products of physiological importance contain nitrogen rings, and of these, one of frequent occurrence is the glyoxaline complex (LIII), the chemistry of which we owe to Pyman and his co-workers.



(LIII.)

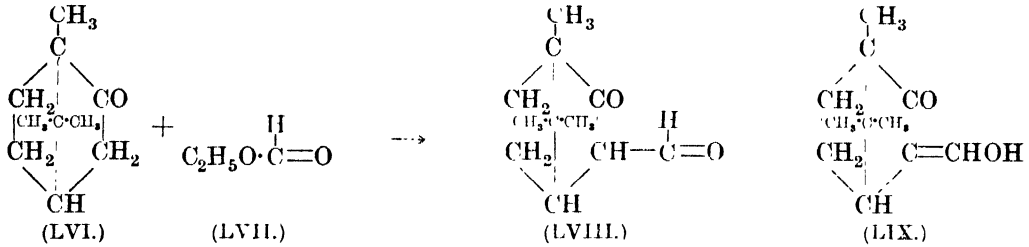
(4) The Meaning of Tautomerism

Organic chemists of the last century were often astonished to find that, when they set out to prepare certain compounds by known reactions, the products showed quite different properties, and therefore possessed totally different structures from those expected. Thus, when vinyl

bromide (LIV) was acted on by potassium hydroxide, instead of the expected product, vinyl alcohol (LV), acetaldehyde (XLVI) was obtained :

$$\underset{\text{(LIV.)}}{CH_2{=}CHBr} + KOH \longrightarrow \underset{\text{(LV.)}}{CH_2{=}CH{\cdot}OH} \longrightarrow \underset{\text{(XLVI.)}}{CH_3{-}\overset{H}{\overset{|}{C}}{=}O}$$

Similarly, when camphor (LVI) was treated with ethyl formate (LVII) and a reagent capable of removing alcohol (sodium), the product was not the expected aldehyde (LVIII), but an acidic substance which undoubtedly had the structure (LIX) :



(LVI.) (LVII.) (LVIII.) (LIX.)

No trace of vinyl alcohol can be isolated in the first reaction, and none of aldehyde in the second, although there can be no question that they are the first products formed in each case. We are therefore faced with the fact that when a hydrogen atom is attached to the terminal atoms of the system C—C=O it can assume either the position CH—C=O or C=C —OH, and that the actual place occupied will depend on the structure of the rest of the molecule. It is evident that vinyl alcohol and hydroxymethylene camphor represent two extreme cases in which the molecular conditions determine definitely the position which the hydrogen has to assume, but it is to be supposed that intermediate between these there will be a number of instances in which the tendency to assume either position will not be so marked, and, in consequence, there will be produced equilibrium mixtures of both forms, the quantity of either individual depending on the actual conditions present. Thus ethyl acetoacetate can have either form (LX) or form (LXI) and experiment shows that, under normal conditions, the liquid substance is composed

$$\underset{\text{(LX.)}\ \text{Keto.}}{CH_3{-}CO{-}CH_2{-}COO{\cdot}C_2H_5} \qquad \underset{\text{(LXI.)}\ \text{Enol}}{CH_3{-}C(OH){=}CH{-}COO{\cdot}C_2H_5}$$

of approximately 2 per cent. of the hydroxy(enol)-modification, and 98 per cent. of the keto-form, and that an alteration in the physical conditions leads to an alteration in the composition of the mixture. The general phenomenon is known as " tautomerism," and is of very frequent occurrence among organic compounds. It is shown by every system which has the general structure HA—B=C, where A, B, and C may be any suitable elements, for example, the following systems have been shown to exhibit tautomerism :

C—C=C	N—C=N	C—N=N
N—N=N	N—C=O	C—N=O
C—C=N	O—C=O	N—N=O
C—C=O	C—N=C	O—N=O

It is, of course, evident that when the substance is a pure solid and has a definite melting point it must represent one individual. It is only when this solid is dissolved, or when it is melted, that tautomerism ensues and the equilibrium mixture is produced.

Before it was understood, this simple phenomenon of tautomerism caused endless trouble among investigators. It was clear that substances such as acetaldehyde and hydroxymethylene camphor possessed the structures assigned to them, because the former gave the reactions of an aldehyde and the latter those of an unsaturated alcohol, but when it came to determining the structures of compounds such as ethyl acetoacetate, which reacted both as a ketone and an unsaturated alcohol, great difficulty was experienced in classifying them.

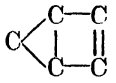
Regarding the mechanism of tautomeric change and the conditions in the molecule which control it, little is known at present. It has, however, been proved that in the three-carbon system there is an intermediate state in which the mobile hydrogen atom can be shown to be present on the central carbon atom of the system :

$$HC{-}C{=}C \qquad C{-}\underset{(H)}{C}{-}C \qquad C{=}C{-}CH$$

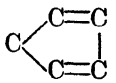
It follows that, in all probability, all tautomerism of this kind is effected through a similar intermediate state and that the keto-enol change, for example, should be represented thus :

$$HC{-}C{=}O \qquad C{-}\underset{(H)}{C}{-}O \qquad C{=}C{-}OH$$

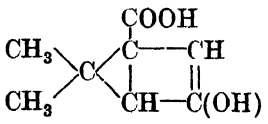
The tautomerism referred to above involves the movement of a hydrogen atom (the mobile hydrogen atom); there is also another kind which is unaccompanied by any such movement and depends for its occurrence entirely on a change in the distribution of valencies in a ring system. For example, it has been found that a substance having the bridged-ring formula (LXII) reacts, not only as if it had this structure, but also as if it had the doubly unsaturated formula (LXIII) :



(LXII.)



(LXIII.)



(LXIV.)

It will be observed, by reference to the actual compound investigated (LXIV), that the change from one individual to the other takes place without the movement of any atom or group. This kind of tautomeric change, which has been named " intra-annular tautomerism," appears to be of very wide occurrence among organic ring compounds. Reference will be made to it again when the chemistry of benzene is being considered, as it is probable that the example given above represents, in its simplest form, the same kind of intramolecular change as that which leads to the special properties of this hydrocarbon and its derivatives.

(5) The Chemistry of Benzene

The hydrocarbon benzene was discovered by Faraday in the coal tar distillate, and a determination of its empirical formula gave figures corresponding with the expression C_6H_6. When it is remembered that a fully saturated hydrocarbon, for example, ethane, C_2H_6, has the general formula C_nH_{2n+2}, and the unsaturated condition of ethylene C_2H_4, and acetylene, C_2H_2, are represented by the formulæ C_nH_{2n} and C_nH_{2n-2} respectively, it will be realised that the empirical formula of benzene, C_6H_6, or C_nH_{2n-6}, must represent a degree of unsaturation considerably greater than that of acetylene itself. But the chemical reactions of benzene are not those of an unsaturated substance. It is true that it forms addition products, with, for example, hydrogen, just as ethylene forms an additive product under similar conditions, but there are two points of fundamental difference between the compounds produced.

The equations representing the reductions in each case may be given as under:

$$C_nH_{2n} \text{ or } C_2H_4 + H_2 \longrightarrow C_2H_6 \text{ or } C_nH_{2n+2}$$
$$C_nH_{2n-6} \text{ or } C_6H_6 + 3H_2 \longrightarrow C_6H_{12} \text{ or } C_nH_{2n}$$

and it is at once clear that, while ethylene leads to a fully saturated substance, C_nH_{2n+2}, the reduction of benzene stops at a stage which yields a substance, the empirical formula of which, C_nH_{2n}, shows it to be as unsaturated as ethylene itself. There must therefore be some essential difference between ethylene, C_2H_4, and the hydrocarbon C_6H_{12}.

Again, it has been mentioned already that unsaturated compounds such as ethylene are definitely less stable than saturated substances like ethane. It is not to be expected therefore that ethane would be converted into ethylene on oxidation in accordance with the equation:

$$C_2H_6 + O \longrightarrow C_2H_4 + H_2O$$

and, as a matter of fact, this change cannot be carried out experimentally. Yet this is precisely what happens in the case of the hydrocarbon C_6H_{12}, for, on treatment with an oxidising agent, it is transformed into benzene:

$$C_6H_{12} + 3O \longrightarrow C_6H_6 + 3H_2O$$

It follows then that benzene must be definitely more stable than its reduction product C_6H_{12}, and that there must be some fundamental difference between benzene and other unsaturated substances, for which graphical expression must be found just as with other carbon compounds.

A study of the chemistry of benzene supplies certain data for consideration, the more important points being as follows:

(1) All six hydrogen atoms in benzene are of equal value, that is to say, there is only one mono-substitution derivative of benzene (*e.g.* phenol, C_6H_5OH). This can be proved experimentally, and shows that, like methane, which has four equal hydrogen atoms and requires a graphic formula (the tetrahedron) having at least four planes of symmetry, the graphic formula representing benzene must have at least six planes of symmetry.

(2) There are three di-substitution derivatives of benzene, that is, when one of the hydrogen atoms is replaced, there are three positions into which a second substituting group or atom of the same kind can enter.

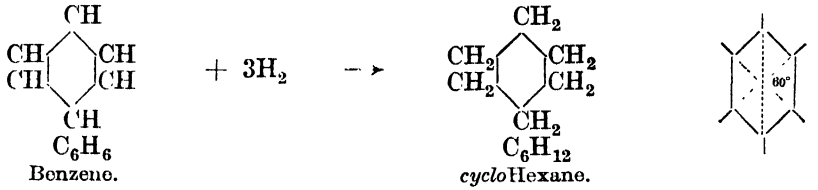
(3) In the same way, there are three tri-substitution derivatives and three tetra-substituted derivatives containing the same groups.

(4) It is only when five like groups or elements enter into the molecule of benzene that one form (isomer) exists, consequently a penta-substitution product of benzene containing like substituents possesses no plane of symmetry.

(5) On the other hand, it has not been found possible to isolate any derivative of benzene. containing a single nucleus, in optically active forms, and, consequently, the mirror image of any compound derived from the hydrocarbon must be superimposable on its object, that is to say, every derivative of this kind must contain a plane of symmetry.

One salient fact which emerges from these, apparently contradictory, statements, is that any graphic formula for benzene must be uniplanar, that is to say, it must be two-dimensional, the third dimension, in other words, the plane of the paper, representing the plane of symmetry which is always present.

A clue to the formula of benzene is supplied by a consideration of the structure of the hydrocarbon, C_6H_{12}, which is formed from it on reduction with hydrogen. This substance, as already stated, has the same general formula as ethylene, namely, C_nH_{2n}, but, unlike ethylene, it obviously contains no double bond. The only way in which this can be expressed is to join two carbon atoms of the six so as to form a ring, and the close relationship between the hydrocarbon C_6H_{12} and benzene, the formula of which must have, at least, six planes of symmetry, makes the regular hexagon the only possible form capable of representing both substances, thus :



If, then, one had to express the formula of benzene from the facts to hand one would say :

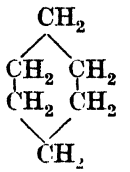
(*a*) That the six carbon atoms of benzene were arranged at the angular points of a regular hexagon.

(*b*) That each carbon atom had one hydrogen atom attached to it.

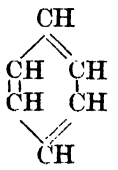
(*c*) That the carbon atoms were in the same plane, and that the valencies carrying the hydrogen atoms emerge from the ring in the same plane as the ring, and at angles to one another of 60° as shown.

This would be an adequate expression of the structure of benzene were it not for the fact that chemists, by long custom, have come to regard the element carbon as tetravalent, whereas, in the above formula for benzene, it is trivalent. It is true that they have had to admit that in some cases carbon is divalent, as in carbon monoxide, C=O, and in fulminic acid, C=NOH, and also that it can act apparently as a trivalent element, as in the triphenylmethyl compounds of Gomberg, $C(C_6H_5)_3$, but it has always been possible to point out that the compounds belonging to these classes are definitely unsaturated, and tend to pass into the saturated forms on treatment with suitable reagents. They are not, therefore, in any way analogous to benzene in properties or behaviour.

Thus, there has always been a quite legitimate and reasonable desire to express the formula of benzene in such a way as to show the carbon atoms possessed of their orthodox valencies, and as *cyclo*hexane is formed by the reduction of benzene and is reconverted into it on oxidation, it follows that the simplest formula would be that represented by the expression (LXV). This,

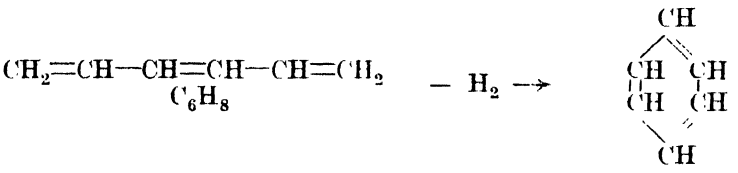


*cyclo*Hexane.



Benzene.
(LXV.)

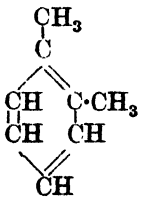
as a matter of fact, is the formula originally assigned to benzene by Kekulé, and is in complete accord with some of the reactions of the hydrocarbon. For example, the formula contains an alternating system of double and single linkages. Benzene should therefore be coloured, just as glyoxal (p. 106) is coloured. As a matter of fact, benzene is an intensely coloured substance, but since the absorption occurs in the ultra-violet region of the spectrum, that is, outside the visible range, it is colourless to the eye. Again, the preparation of the unsaturated open-chain analogue of benzene, which would in accordance with the Kekulé formula, have the structure (LXV), and the comparison of its magnetic rotation with that of benzene by Sir William Perkin,

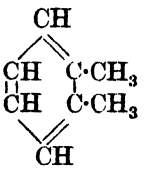


Hexatriene. Benzene.

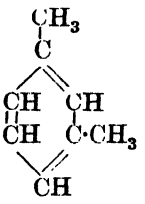
gave figures which correspond with the calculated difference between an open chain compound and the closed ring which would be derived from it by the loss of two atoms of hydrogen.

It is clear, therefore, that the formula originally assigned by Kekulé to benzene must represent its structure, at any rate in one of its phases. But Kekulé himself realised that this formula did not express the facts, because it was evident to him that the occurrence of only three di-derivatives could not be explained thereby. For example, if his formula were correct there would be four di-derivatives when the substituents were the same, namely, two ortho, one meta, and one para, thus :

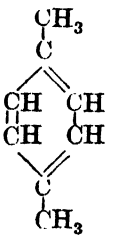




Ortho.



Meta.



Para.

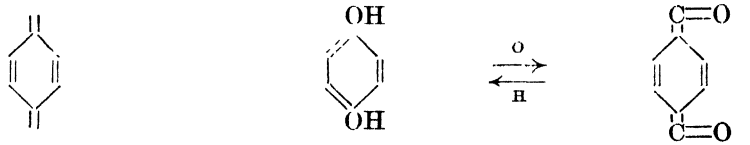
That is to say, there would be two ortho-xylenes (dimethylbenzenes) instead of one as experiment shows to be the case. It was therefore assumed that rapid intramolecular interchange occurred between the two forms (*a*) and (*b*) leading to a dynamic condition, which was afterwards embodied in the Armstrong or centric formula (*c*). As a matter of fact, all the



reactions of benzene, excepting those which lead to additive products, can be expressed adequately by ignoring the fourth valency of the carbon atoms, and writing the formula as a simple hexagon (*e*), and this is the practice universally adopted; the attachment of substituting groups being shown by writing the group at the desired angular point (*d*). In this formula, the presence of the carbon atom originally attached to the hydrogen atom substituted, and of the remaining CH groups around the ring, are assumed. Indeed, such a formula expresses an intermediate state between the two Kekulé dynamic individuals, a state which is perhaps better, although more clumsily indicated, by the Thiele conjugated formula (*f*).

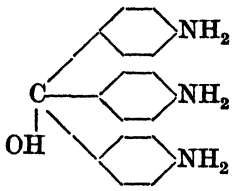
The dynamic conception of the structure of benzene is certainly attractive, and is in agreement with the general views expressed in this narrative regarding the stability of substances which are capable of free motion; it is, moreover, borne out by a consideration of the chemistry of the visibly coloured substances which can be obtained from it.

If the power possessed by benzene to cause selective absorption in the ultra-violet region of the spectrum is due to the peculiar dynamic condition which is expressed by the accepted graphic formulæ, it should be possible, by the formation of derivatives or otherwise, so far to influence the dynamic state as to throw the absorption into the visible range of the spectrum, thus producing substances having visible colour. The great majority of the derivatives of benzene are colourless to the eye, but a considerable number of them possess intense visible colour, and, some years ago, Armstrong suggested that the visibly coloured substances of this series owed their colour to the presence in them of the quinone ring (LXVI). Quinone (LXVIII) itself has a marked yellow colour, and as it is readily formed from the di-hydric phenol hydroquinone (LXVII) on oxidation, and is itself readily reconverted into hydroquinone on reduction with hydrogen, the relationship between the two is quite clearly defined:



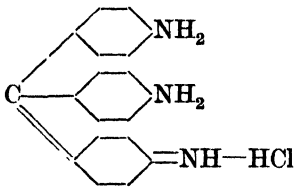
(LXVI.) (LXVII.) (LXVIII.)

The quinone theory of colour, at first received with considerable hesitation, has now become the fundamental principle on which the chemistry of the coal-tar colours is based. For example, the change from the visibly colourless base of magenta to its intensely coloured hydrochloride is now generally accepted as taking place in accordance with the scheme:



Magenta (base).
Visibly colourless.

+ HCl



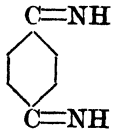
Magenta (salt).
Visibly coloured.

+ H_2O

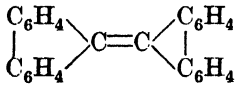
The quinone theory does not imply :

(*a*) That all derivatives of quinone are coloured, or
(*b*) That all coloured derivatives of benzene possess a quinoidal structure.

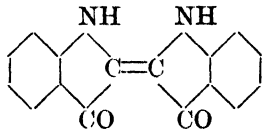
Some derivatives of quinone imide (LXIX), for example, are not visibly coloured, and it is not possible to express the hydrocarbon bidiphenylene ethylene (LXX) which is yellow, or indigo (LXXI) which is blue, as quinone derivatives.



(LXIX.)



(LXX.)



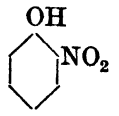
(LXXI.)

The view to be taken is therefore as follows :

(1) That it is possible to throw the ultra-violet absorption of benzene into the visible region of the spectrum by the formation of suitable derivatives.

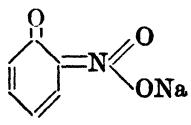
(2) That one of the structures illustrating this change is the quinone ring. It does not necessarily follow that all quinone derivatives are visibly coloured, as some of them may retain the ultra-violet absorption of the parent hydrocarbon. Neither does it follow that all derivatives of benzene which possess colour contain the quinone nucleus, because other molecular groupings, such as, for example, those present in indigo, also throw the absorption into the visible region.

The rather difficult question of the nitrophenols is a case in point. Everything appears to be clear as regards the ortho- and para-compounds, and their passage from the visibly colourless or faintly coloured parent substances (LXXII) and (LXXIII) into the strongly coloured sodium salts (LXXIV) and (LXXV) can be represented adequately by the scheme :

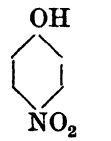


(LXXII.)

→

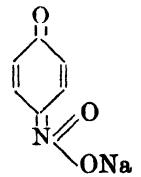


(LXXIV.)
o-Quinone derivatives.



(LXXIII.)

→



(LXXV.)
p-Quinone derivatives.

But the difficulty arises with the meta-compound (LXXVI), the sodium salt of which (LXXVII) is also coloured. Although not ruled out as impossible, it is, at any rate, difficult to express the quinoidal condition in the meta-series, and, as a matter of experimental fact, no one has as

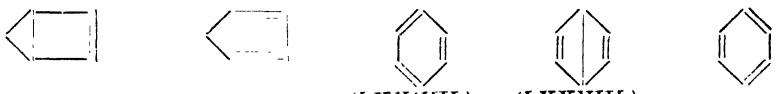
yet succeeded in obtaining definite evidence of the existence of the meta-quinoidal state. It is possible therefore that the colour of these sodium salts of the nitrophenol may be due to other than quinoidal conditions, and it must be remembered, in this connection, that *o*-nitrophenol itself has never been obtained colourless.



(LXXVI.) (LXXVII.)

m-Quinone derivatives.

There is some reason to suppose that there is another intermediate state between the two dynamic individuals of the Kekulé formula, by which certain definite properties of benzene can be more adequately expressed than by the centric formula, which is admittedly only a compromise. For example, the occurrence of ortho- and para-derivatives together seem to show that these positions are quite distinct from the meta-state. Moreover, the formation of numerous derivatives associated with the para- and ortho-series seems to render the assumption of some definite link between the para-positions essential. Intra-annular tautomerism has already been described (p. 115), and it will be seen, on examination, that there is a close connection between the two individuals mentioned and benzene, if it is assumed that an intermediate form (LXXVIII) has a para-linkage.



(LXXVIII.) (LXXVIII.)

This formula (LXXVIII) is the one which was originally proposed by Sir James Dewar as representing the structure of benzene. This, of course, it cannot do any more than either one of the Kekulé individuals can, because two ortho-derivatives are also required by the Dewar formula. But the assumption that this form is a phase in the passage from one Kekulé individual into the other supplies an explanation of many facts hitherto unexplained. Moreover, the recent synthetic work of Ingold shows conclusively that when a substance is produced which, by its mode of formation, must have the Dewar formula, it is found to be a derivative of benzene.

The Aliphatic and Aromatic Divisions.—The derivatives of benzene are prepared through the nitro-compounds and the sulphonic acids :

$$C_6H_5—H + HO—NO_2 \longrightarrow C_6H_5NO_2 + H_2O$$
$$C_6H_5—H + HO—SO_3H \longrightarrow C_6H_5SO_3H + H_2O$$

whereas those from ethane or ethylene are formed from the halogen derivatives. This in itself constitutes a difference which has caused the benzene derivatives to be classed as " aromatic " compounds and the other series as " aliphatic " compounds. The source of the hydrocarbons and bases of the aromatic series is the coal-tar distillate from which some 300 definite substances have been isolated. Chief among these are the hydrocarbons benzene, toluene and the three xylenes, naphthalene and anthracene, substances which are constituted much as benzene.

They form the parent substances of a vast number of technical products such as drugs, perfumes, explosives, dyes, etc.

MILESTONES IN ORGANIC CHEMISTRY

By Henry E. Armstrong, F.R.S.

The year (1865) of the introduction of the Sprengel mercury-fall pump and of the closed 'ring' formula of Benzene by Kekulé—both devised in London—is that in which the writer began to study chemistry. He is, therefore, able to survey a period of critical importance, during which chemical method and knowledge have been developed to an extent inconceivable at the outset of his career. A brief reference to some of the outstanding events may not be without interest, at a time when the upgrowth of chemical science is under notice.

At the beginning of the period, with the aid of the pump, Frankland and he (1866–67) had developed the vacuum combustion method of determining carbon and nitrogen simultaneously, which Frankland, as a member of the Rivers Pollution Commission, forthwith applied to the study of the organic matter in drinking water and so brought about a revolution in our English water supply, placing us ahead of all the world by making England a country in which water was a safe drink.

Now, at the close of the period, with the aid of the *X*-ray bulb, an instrument which is a direct descendant of the mercury pump and the Crookes' Radiometer, English physicists are not only verifying the structural formulæ devised, in the interval, by chemists but are able both to trace in the diamond the embryonic ring-structure of benzene and even to state the dimensions of the hydrocarbon-complex in Angström units. Only the few can appreciate the vast output of intellectual energy and of laboratory work which this achievement has involved, let alone the actual cost.

In 1865, the change from O = 8 to O = 16, C = 6 to C = 12 was not yet complete; only the lower scale of weights was to be found in most of the text-books. No clearly defined method of ascertaining atomic weight was in vogue—we had not then learnt to apply Avogadro's theorem to the determination of molecular weights, as the necessary final step towards determining atomic weights, though we talked much of two-volume formulæ. We were not even fully persuaded of the existence of atoms. Even in 1874, in the writer's *Introduction to Organic Chemistry* (then defined as *The Chemistry of Carbon and its Compounds*), the neutral term 'unit-weight' was used, instead of atomic weight—under the influence of Williamson's conservatism—and 'two-volume formula' as the equivalent of molecular formula.

Kekulé's formula of benzene was not even given in the book; although the peculiar character of benzene was referred to and a good deal was said of the isomeric derivatives, no attempt was made to discuss the structure of the hydrocarbon. The fact is, the attention of chemists was not specially attracted to the peculiar problems of constitution the benzene derivatives afforded, until the appearance of Körner's masterly monograph, in 1874—when the value of the symbol became obvious. Meanwhile, interest had been further excited by the recognition of naphthalene and anthracene as analogous to benzene in structure and especially by Graebe's work on the quinones and the demonstration by Graebe and Liebermann of the relation of alizarin to anthracene. The study of the structure of benzene derivatives was actively pursued at this time—during the 'seventies. The writer was able to discuss the subject comprehensively in an article on Phenols in the second supplement to Watts' Dictionary (1875) and, more fully, in the third volume of Miller's Chemistry (Organic Chemistry), published in 1880.

A few years later, he devised the *Centric* symbol which gives complete expression to the character of benzene. Recently, Barlow and he have constructed an equivalent geometric model in which the spatial peculiarities of the hydrocarbon and its derivatives are simulated.

The organic chemist of the past half-century has been far more than the mere interpreter of Nature: he has displayed an entirely marvellous constructive activity and developed powers far beyond those of Nature; perhaps the most striking result of his enquiries is the discovery of the limits imposed upon the organism and the relative simplicity of what may be termed *Natural Chemistry*. The advance in organic chemistry is only matched by that of our Ironclad Navy, including that of motor mechanism, which began about 1860.

The fundamental discovery is that made by Wöhler, in 1828, in showing that *Urea*, the characteristic crystalline constituent of urine—that in which most of the nitrogen in our food is regularly voided, to the extent of about an ounce a day, at least—could be produced by entirely artificial means, *synthetically*. Up to that time, the opinion prevailed that the compounds characteristic of animal and vegetable activity were formed under the influence of a vital agency. All such belief has long since been abandoned, although it is recognised that there are peculiar formative influences at work within the organism which entail a stringent selection being made from among the innumerable possibilities. The chemistry of living things, in fact, is a far more select and simpler chemistry than that of the laboratory; in some ways, the chemist's power transcends that of Nature. Nature works to pattern, the chemist almost as a licensed libertine.

The importance of Wöhler's discovery was manifold. The doctrine of *Isomerism* was its direct outcome, as was also that of reversible isomeric change or *Metamerism*—both conceptions which simmered long in the minds of workers before reaching their modern development. Wöhler sought to prepare the ammonia salt of cyanic acid; instead, he obtained the highly stable, slightly basic substance, urea: although he produced the salt primarily in solution this passed rapidly over into urea. The elementary composition of the two compounds is the same but they differ in structure: compounds so related are termed *isomeric*. If silver nitrate be added to a solution of urea in the right proportion and the liquid be heated, the urea is almost entirely reconverted into (silver) cyanate. The term *metameric*, which Berzelius aptly applied to isomeric substances thus reversibly related– not only convertible into one another but usually present together in sensible amounts in equilibrium in solution—is practically the equivalent of the more familiar term metamorphic, the use of which, however, is confined to mineralogy. Urea, it may be added, is very easily and rapidly converted into the ammonia salt of carbonic acid by means of the *enzyme* Urease, which is particularly abundant in the Soja bean and also present in soil micro-organisms.

Forty years after Wöhler's discovery, Basarow obtained urea by heating the ammonia salt of carbonic acid in sealed tubes—that is to say practically from two molecules of ammonia (NH_3) plus one of carbonic acid (CO_2). The writer was present in the Leipzig laboratory when this happened and saw the first specimen thus produced, as it crystallised from solution. Meanwhile we have learnt to manufacture ammonia from the air. It now seems probable that, after a further interval of more than fifty years, Basarow's method may be made a large-scale process and that urea may take its place as a primary nitrogenous fertiliser. It has the great advantage that it is wholly available, carrying neither acid (as does an ammonia salt) nor alkali (as does a nitrate) into the soil. At present, agriculturists are not agreed, however, that it can be used under all farming conditions. Should this be the case, Wöhler's discovery will have proved to be the alpha and omega of scientific achievement. We shall doubtless know by the time its centenary is reached.

One hundred years ago, next year, Faraday discovered benzene, in the laboratory of the

Royal Institution, Albemarle Street, London, obtaining it in the pure, crystalline state, as we know it to-day. Benzoic acid, prepared by sublimation from Gum Benzoin, had long been known but Scheele, in 1775, was the first to separate it by a chemical process. Mitscherlich obtained Faraday's hydrocarbon from benzoic acid in 1833, when Liebig christened it *Benzol*. Laurent, describing its formation from phenyl alcohol (phenol) in 1843, was the first to propose the name *Phène* or *Benzène*. Laurent is thus the father of the terminal *ene* now applied to all hydrocarbons other than the paraffins. Mitscherlich prepared nitrobenzene in 1834; this was reduced by Zinin in 1841; Hofmann, in 1843, showed that the reduction product was identical with the *Anilin* obtained by Fritsche, in 1841, by distilling indigo with potash.

During the twenty years Hofmann was Professor of Chemistry in the Royal College of Chemistry, Oxford Street, London (1845–65), he made aniline his main subject of study. The method of separating benzene from coal-tar was worked out in his laboratory by Mansfield (1849). In 1856, his pupil Perkin discovered the first artificial aniline dyestuff, *Mauve*, an event soon followed in France by Verguin's discovery of Rosaniline, as it was subsequently termed by Hofmann. Nicholson (of Simpson, Maule and Nicholson), also a pupil of the Royal College, first brought the manufacture of this wonderful dyestuff to perfection. Hofmann devoted himself to its study, showing that Lyons blue was its triphenylated derivative and prepared Methyl Violet by methylating it, etc. Finally, Emil and Otto Fischer were able to prove (1876) that Rosaniline was a triphenylmethane derivative and thus put system into the most fascinating of all the chapters on colour chemistry.

Not a little pioneer work in the other chapters has been done in this country. Perkin was joint discoverer with Graebe and Liebermann of methods of preparing the madder colours from anthracene and was the first to manufacture alizarin successfully. Witt, working with Williams, Thomas and Dower at Brentford, was the first to manufacture acid azo-dyestuffs (the Tropæolins). Although the diazo-compounds were discovered by Peter Griess, when a student at Marburg, his life-long study of the group was carried out at Burton-on-Trent. The late Professor Meldola is known as the discoverer of several useful colours, as is also A. G. Green. Lastly, A. G. Perkin, at Leeds, has contributed greatly to our knowledge of the natural flavone colours. Flavone itself, the parent member of the group, was first shown to occur naturally and isolated from *Primula* species by Hugo Müller, working in the laboratory of the Royal Institution. By our studies during more than a dozen years of the di- and tri-derivatives of naphthalene, Wynne and the writer have provided the industry with a complete series of reference compounds. Our continued failure to hold and develop the manufacture of dyestuffs is clearly in no way due to inability of British scientific workers to master the problems of the industry: beyond question, it is simply a consequence of our rooted objection to make systematic use of science, in the service of industrial enterprise—of the inability of our commercial class to appreciate and apply scientific method. Unless science be allowed to play its balanced part in industry, to speak with authority, our chance, in the future, of holding our own against the competition of the world, must be small.

Foundations have been laid in not a few fields in this country. Thus Gladstone, Wright, Tilden and the writer were workers with the Turpentines and Essential Oils in the 'sixties and 'seventies, before Wallach began his exhaustive survey of the group—using Tilden's nitroso-chloride as fiducial mark. Later on, von Baeyer and Tiemann made important contributions to our knowledge of the structure of terpenes and their derivatives. On the synthetic

side, however, the honours are in our hands, owing to the masterly constructive ability shown by W. H. Perkin, jun., in his synthetic studies in the group. The work of the school has culminated in the synthesis of rubber—though by methods which are not likely ever to rival those of Nature; also it has led to the development of a great artificial perfume industry in Germany: again, we laid the foundation: Perkin, sen., made coumarin—the odoriferous principle of the Tonka bean and of Woodruff—artificially in 1867.

Matthiessen, with Carey Foster and Alder Wright, following Anderson, laid the foundation of the study of the opium alkaloids in the 'sixties. The subject then passed into German hands, but in recent years the work of Perkin, jun., on alkaloids has rivalled even that of the great Munich school.

The writer began work with camphor, at the London Institution, early in the 'seventies and dared to doubt the accuracy of Kekulé's interpretation of its constitution: of course, no attention was paid to such impious questioning of authority; still, it has been proved to be sound. The value of the work done by our English camphor school is generally recognised; with it are to be associated the names of Forster, Kipping, Lapworth, Lowry, W. H. Perkin, Pope and J. F. Thorpe. In Pope's hands, the camphorsulphonic acids have been tools of astounding efficiency, in proving that several of the elements, notably nitrogen, sulphur and tin, simulate carbon in giving rise to asymmetric, optically active compounds—a result of the greatest theoretic importance. Werner's success, in resolving many of the complex metal-ammonia compounds into optically active components, was due largely to his use of the weapon forged by Pope in our South Kensington laboratory.

The brewing industry has been of surprising assistance to the progress of chemical science in this country, apart from the fact that modern preventive medicine starts from the enquiries made by Pasteur in aid of the fermentation industries. Griess, of diazo-fame, was chemist to the Allsopps; O'Sullivan, the rediscoverer of maltose, was chemist to Bass & Co.; Horace and Adrian Brown also worked in Burtonian service. O'Sullivan's study of the mashing process——of the action of diastase on starch—and then of the action of invertase on cane-sugar, gave impetus to the study of carbohydrates and of enzymic action at a time when such matters were in no way attractive to chemists. He was followed by the Browns. Not a little was done in the writer's laboratory, especially on enzymic problems—but this has been systematically overlooked, not being incorporated in a student's text-book, in an age when original literature is but little consulted.

The work of Emil Fischer and his school on the Sugars has very properly been regarded as so masterly as to put that of all others in the shade, the more as it has been followed by equally important, though less complete work on Proteins—a far more difficult chapter, be it noted. It is impossible to over-rate the value of the example Fischer has set, for all time, by his systematic attack on the problems these two great groups of natural materials afford: they are the foundation stones of our being. Fortunately, the Purdie-Irvine school is now working in the same spirit, attempting, with marked success, to decipher the structure of starch and cellulose, in many ways a more difficult task than that undertaken by Fischer.

Speaking of cellulose, the writer recalls the difficulty with which a grant was secured from the Royal Society for Mr. Cross for the enquiry which led him to the discovery of Viscose, now developed into an industry from which millions and millions have already been gained.

Many other milestones should be mentioned were space available: enough will have been said to make clear the importance of the organic branch in chemistry.

We are at the moment acclaiming the re-entrance of the physicist upon our stage. He is ascertaining the spacing of the molecules in crystalline solids, with the aid of *X*-rays. The story he is telling is but the story we have long since told—with the aid of little more than the conceptions of valency introduced by Frankland in 1852, supplemented by the van't Hoff-Le Bel theorem in 1875. The rigid logic of our chemical method, as applied to organic compounds, is thus brought into prominence and to some extent appreciated. Our convictions rest upon the overwhelming odds in our favour—we are able to bet in terms of several hundreds or even thousands to one, having wagered and won with such uniform success during a period of over fifty years. Hence it is, that we can speak *of a science* of organic chemistry. On the mineral side, there is no such certainty, as we are unable to give any particular odds with certainty, let alone the long odds of the organic branch. We can't even say how so simple a substance as sulphuric acid is structurally compounded. Now that we have trust in *X*-rays, through organic chemistry, we shall have faith in their readings of mineral character—so long as they do not involve assumptions which are serious infractions of our rules. Here, as elsewhere, the absolute interdependence of chemical and physical enquiry is brought clearly into view. The future is with the two sciences working in close co-operation.

THE CHEMISTRY OF COLLOIDS

By WILLIAM CLAYTON, D.Sc.

THE real study of Colloids began with an Englishman, Thomas Graham, about 1861, and though but a young branch of science, its industrial applications are exceedingly widespread and of great and increasing importance. In the development of the present position of Colloid Chemistry, British men of science have played no small part, while the recent opening of the Thomas Graham Colloid Laboratory at the University of Manchester is one sign of the keen interest displayed in Colloids to-day.

To define what is implied by the term Colloids necessitates some discussion, inasmuch as the modern meaning is much wider than that of Graham, and, indeed, includes his definition only as a special case. The development of the modern interpretation of Colloids is a fascinating theme, the detailed elaboration of which is beyond the scope or dimensions of this article. At bottom, Graham's definition is chemical, the modern is physical, though even now the former of the two schools of thought has its supporters.

Graham's classical papers on "Liquid Diffusion Applied to Analysis" and "On the Properties of Colloidal Silicic Acid and other Analogous Colloidal Substances" dealt with the question of the diffusion in solution of such substances as hydrated silicic acid, hydrated alumina, starch, dextrin, gums, caramel, tannin, albumen, gelatin, and vegetable and animal extractive matters. In Graham's own words: "Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous nature of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical reactions. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of this class as colloids,* and to speak of their peculiar form of aggregation as the colloidal condition of matter. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as crystalloids. The distinction is, no doubt, one of intimate molecular constitution."

Substances of a colloidal character were found by Graham to admit of separation from the liquid (usually water) in which they were apparently dissolved, by what he termed dialysis, *i.e.* a parchment membrane would permit diffusion of the solvent, but would not allow the passage of the colloid. On the other hand, typically crystalline bodies like sugar and inorganic salts would readily diffuse through such a membrane. Graham was thus led to conclude that the units in solutions of colloids were composed of larger molecular aggregates than were present in solutions of crystalline substances. In a sense, he believed that colloids were polymerised molecules; this polymerisation differs from true chemical polymerisation in that the colloidal condition is more or less labile, being dependent on external conditions and on the previous history and the age of the colloid solution.

Though Graham's colloids are characterised by the complexity of the molecular structure, the converse is by no means true, many substances of complex composition being known which are in no sense colloidal. Again, certain compounds may occur in true (molecular) or homogeneous solution in some solvents, and give colloidal or heterogeneous solutions with other solvents. Thus tannic acid gives a true solution in alcohol, and a colloidal solution in water,

* Greek, Kolla = glue.

whilst tetra-amylammonium iodide gives a colloidal solution in benzene and a true solution in acetone.

The present view of colloidal solutions, based on an enormous mass of research work, is that there is no distinction such as " colloids " and " crystalloids," but that the distinction is between matter in the " colloid state " and in the " crystalline state." Substances, which to Graham were typically colloidal, *e.g.* albumin, have since been obtained in crystalline form, whilst typically crystalline substances, *e.g.* common salt, have been obtained in colloidal solution.

The new view on colloidal solutions dates from 1898, when Bredig and Zsigmondy independently produced colloidal solutions of metals, the former by electrical methods, the latter by chemical reduction. These classical investigations produced colloidal solutions of metals, apparently as clear, transparent liquids, but the metal would not diffuse through a dialysing membrane. In 1903, Siedentopf and Zsigmondy, with the aid of their ultra-microscope, showed that the metal was not in molecular solution, but in an exceedingly fine suspension, the metal particles having diameters between 10 and 500 $\mu\mu$.* The colloidal state has now been shown to be a transition state between that of molecular solutions and coarse suspensions, *i.e.* a substance is said to be in the colloidal condition when the dispersed particles range from 0·1 μ to 1·0 $\mu\mu$ in diameter. Such particles will pass through filter-papers, are retained by a dialysing membrane, and are not analysed by ordinary microscopic examination.

On this basis, the colloidal state is possible for any substance, and merely represents a convenient classification for a transitional state of subdivision or dispersion. Wonderful experimental support to this conclusion has been given by P. P. von Weimarn, who has prepared colloidal solutions of hundreds of substances. Particularly striking is his formation of precipitates in all degrees of fineness.

So far, we have tacitly assumed the case of the dispersion of a solid in a liquid medium, but it is obvious from the definition of the colloidal state that the dispersed substance may also be a liquid or a gas, and may be dispersed in another liquid, a solid, or a gas.† Recognising this, Wo. Ostwald proposed the following classification of colloid systems :

Dispersed substance.	Medium in which dispersed.	Examples.
Solid	Solid	Carbon particles in iron. Gold in ruby glass.
Solid	Liquid	Colloidal solutions of metals, gelatin, starch, etc.
Solid	Gas	Smoke. Fine dust. Fumes.
Liquid	Solid	Certain minerals.
Liquid	Liquid	Emulsions.
Liquid	Gas	Fog, mist, clouds.
Gas	Solid	Solidified froths, *e.g.* pumice.
Gas	Liquid	Froths and foams.

From this table will be evident the wide scope of colloid chemistry and how extensive is the range of its possible industrial applications.

* $\mu\mu$ = 1 millionth of a millimetre.

† The case of gas dispersed in a gas does not, of course, belong to the study of colloidal systems, gases mixing freely to homogeneous systems.

The point now to be emphasised is that in all colloidal systems a great development of surface has taken place. When a given mass of substance is divided up, the surface area exposed becomes greater and greater as the process of subdivision (*e.g.* dispersion in a medium) is continued. As a consequence, surface forces come into play, their magnitude and effects becoming of greater importance with increased dispersion. This leads to the very flexible, purely physical, definition of a colloid system as one consisting of at least two phases, one of which exposes a great surface area. Hence colloid chemistry and physics deal with such systems as films, foams, bubbles, grains, drops, mists, jellies, and all cellular formations such as skins, paper, peat, wood, and animal and vegetable structures generally. Of great importance is the study of the surface tension at the boundary between the dispersed substance and the medium surrounding it.

Within recent years, this aspect of colloid chemistry has received special attention, and remarkable advances have been made in our knowledge of surfaces, boundaries, or interfaces, in relation to the interfacial tension and allied phenomena.

Certain views of Hardy (1912) in this country were later developed and expanded by Harkins and Langmuir in America, working independently on somewhat different lines. The earlier view of surface tension due to Laplace is that the peculiar condition of tension at the surface of a liquid is due to the molecules in the bulk of the liquid being attracted on all sides, whilst those at the surface are subjected to an unbalanced attraction, so that there is an inward pull on the surface molecules.

The new notions are concerned with the *structure* of liquid surfaces in relation to surface tension. The basic idea involved is that in the surface of a liquid in contact with air, the molecules are orientated or marshalled in definite order, and the main factor determining the surface tension is the structure of the surface layer of atoms. The surface molecules are so orientated that their most active portions are drawn inwards, so that the least active portions of the molecules (orientated towards the vapour phase) constitute the surface layer. Thus the least active portions of the molecules, and the manner in which these are arranged in the surface layer, determine the surface energy of a liquid. For example, in the liquid paraffin series of hydrocarbons, the molecules are so arranged that the CH_3 groups at the ends of the hydrocarbon chains form the surface layer, no matter how long the chain may be. Experiment shows that the whole series, from hexane to molten paraffin, has practically the same surface energy. For organic liquids in general, the active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, are orientated towards the interior of the liquid, as are also groups which contain N, S, O, I, or double bonds.

In the case of two pure liquids in contact, their like parts orientate towards each other, the separating boundary surface thus possessing a definite packing or structure of molecules. Thus, when an organic liquid and water make an interface, the organic radical turns towards the organic liquid, and the active or " polar " group towards the water.

The new ideas of surfaces have proved very useful in certain technical operations. In this connection, the production of emulsions, *e.g.* pharmaceutical emulsions, margarine, lubricants, the practice of ore separation by flotation, and the action of certain oils and fats as shortening agents in bread-, cake-, and biscuit-cooking, have been regarded from a new angle with interesting results.

The remarkable extension of surface area in colloidal systems leads us to consider another phenomenon of great interest both in theory and in technical applications. This phenomenon is concerned with the change in concentration of a substance which occurs at the boundary

surface between the substance and another phase. Thus charcoal will remove the colouring matter from certain solutions, *e.g.* dyestuffs, whilst fuller's earth is used to decolorise certain oils. The colouring matter becomes concentrated upon the surface of the charcoal. Similarly, charcoal or silica gel will " take up " large volumes of gases, a fact utilised in the production of high vacua and in gas masks. Such concentration changes due to surface action are grouped under the term Adsorption. The phenomenon of adsorption is responsible for the stability of froths and foams, of emulsions, and of many colloidal solutions, and finds important application in the dyeing industry.

We are now in a position to consider the subject of colloidal systems in their industrial applications. The classification of Ostwald is convenient to use. Various special features characteristic of certain colloidal systems can best be studied as occasion arises, inasmuch as general statements of theory frequently demand important modification in special cases.

Solid Dispersed in Solid.—Certain natural minerals are coloured by the presence of foreign matter in a state of colloidal dispersion, *e.g.* smoky quartz, " beef-steak " rock-salt (coloured red by finely-divided iron oxide). Colloidal gold is the secret of ruby glass, whilst colloidal chromium colours artificial rubies. Ultramarine is believed to be a solid solution of sulphur in a mixture of silicates, borates, etc. It is quite possible that the hardening of steel is a colloidal problem connected with the dispersion of carbon in the steel, and it has been pointed out by Desch that the degree of dispersion of a solid phase in a crystalline medium is a factor of great importance in the study of steels and of other metallic alloys.

Solid Dispersed in Liquid.—The major portion of colloidal systems come in this class, including such cases as colloidal metals; protein solutions; suspensions, slimes and muds; and involving the phenomena of protection, coagulation, sedimentation, flotation, electrical migration, etc. The nature of protein solutions, of soap solutions, and of jellies also comes under this heading.

Colloidal metals are the simplest colloidal systems. The metal may be dispersed by electrical disintegration, or by chemical reduction, the usual dispersion medium being water. Colloidal solutions are usually termed sols, a name due to Graham. Dispersions in water are hydrosols; in alcohol, alcosols; in glycerine, glycerosols; in gases, aerosols, etc. The metal particles are electrically charged, migrating to the anode in an electrical field. Addition of electrolytes coagulates the particles through neutralising the electric charge, the positive ion of the electrolyte being responsible, and its effect being more potent as its valency increases. Thus Freundlich found that to coagulate a sol of arsenious sulphide, the required concentration of a monovalent ion (*e.g.* sodium in NaCl) was 70 times greater than that of a divalent ion (*e.g.* barium in $BaCl_2$) and 560 times greater than that of a trivalent ion (*e.g.* aluminium in $AlCl_3$).

In order to render sols stable towards electrolytes, certain so-called " protective " colloids are added to the solution, *e.g.* gelatin, gums, Irish moss, starch. These latter substances, frequently termed emulsoids, are much more stable towards dilute electrolyte solutions than the metal sols and this stability is conferred on the " protected " sol as a whole. The actual mechanism whereby this stability is given is not yet clear, Bechhold's suggestion that the metal particles receive a " protective envelope " of the added emulsoid being only true in certain instances.

Metal sols are being increasingly used as therapeutic reagents. For example, colloidal iron is given orally for anæmia and chlorosis, colloidal silver for influenza, cystitis, colitis, and bacillary dysentery, colloidal iodine for rheumatism, asthma, and eczema. Colloidal selenium and

colloidal copper are given in intramuscular injection for cases of inoperable carcinoma, colloidal manganese for acne and gonorrhœa.

The rapid and intensive dispersion of substances in water is being studied with enthusiasm to-day, and various so-called colloid mills have been patented. The well-known Plauson mill effects the disintegration of numerous substances in an extremely fine state of subdivision, but in most cases the presence of a protective colloid (technically a " dispersator ") is necessary. The production of colloidal sulphur, and of stable aqueous or oil suspensions of carbon black, ochre, ultramarine, chrome green, litharge, zinc oxide, lithophone, etc., is now a commerical proposition. The paint industry in particular finds a valuable tool in the colloid mill, whilst its application to fillers in the rubber industry is also obvious.

The opposite case to the production of colloidal solutions, viz. the coagulation and sedimentation of undesirable or of valuable suspended matter, is of great industrial importance. Apart from the use of suitable electrolytes to coagulate the suspended colloid particles, specially-designed sedimentation plants are in common use, the well-known Dorr plant being an instance. For water clarification, alum is frequently used; precise control of the acidity of the water is necessary for optimum and economic working. Many stable inorganic suspensions are also flocculated by the addition of organic colloids such as glue or starch, but the theory underlying this practice is still vague.

Three special cases of colloidal systems must now be mentioned, viz. soaps, proteins, and jellies.

The complicated colloid chemistry of soaps and soap solutions has been studied for several years at Bristol University by McBain and his co-workers with great success. A detailed account of the subject is impossible here, but one point of very great interest merits attention. McBain has shown that aqueous soap solutions are the prototype of a great group of colloids, which he calls " colloidal electrolytes." These are really salts, one ion of which is replaced by a heavily hydrated ionic micelle bearing a heavy electric charge (at least 10 negative charges) and having a high molecular weight (due to molecular aggregation of comparatively small molecules). The equivalent conductivity of the ionic micelle is quite comparable to that of a true ion, but may be several times as great as that of the simple ions from which it has been derived.

Conductivity and osmotic data furnish the main evidence for the existence of the ionic micelle in soap solutions. Other colloidal electrolytes, not so thoroughly investigated as in the case of soaps, are protein salts, dyes (*e.g.* Congo Red), indicators, tellurates, and many substances of high molecular weight which can split off a true ion.

The practical side of investigations on soaps deals with the familiar subject of detergent action. Several factors are of importance in detergent action: the soap must be in solution and act as an emulsifying agent, *i.e.* be in the colloidal condition. Such solutions will possess a low surface tension and be capable of wetting surfaces as well as forming non-adhesive colloidal adsorption compounds with tissue, dirt, etc., which will remain in suspension, facilitating washing out.

The proteins, important in biology and in industry, have been investigated by many workers, including Hardy in this country, Loeb and Robertson in America, Pauli in Austria, and Sörensen in Denmark. Procter at Leeds has developed the study of gelatin particularly in relation to leather manufacture and tanning with recognised success.

Briefly, proteins are amphoteric electrolytes, *i.e.* can form salts with either acids or bases, *e.g.* protein hydrochloride and sodium proteinate. The actual hydrogen-ion concentration of the solution in water determines the type of salt produced. At an intermediate point, known

as the isoelectric point, no protein compound forms at all. Thus the isoelectric point for gelatin is at $p_H = 4{\cdot}7$,* and for crystalline egg-albumin at $p_H = 4{\cdot}8$. The isoelectric point is of great importance for colloidal solutions generally, the colloid particles being electrically neutral and showing no motion in an electric field.

The study of proteins in solution in relation to the p_H value is concerned with inter-connected phenomena such as swelling, osmotic pressure, viscosity, and with the unequal distribution of diffusible true ions between protein solutions separated by permeable membranes from external aqueous solutions. The last phenomenon has received detailed investigation by Loeb, who has thereby developed and extended an important theorem thermodynamically derived by Donnan. Donnan's theory of membrane equilibrium is that when a protein solution, *e.g.* gelatin chloride, is separated from an aqueous crystalloid solution by a membrane freely permeable to the ions of the latter but preventing protein diffusion, osmotic equilibrium is characterised by the fact that the products of the concentrations of each pair of oppositely charged diffusible ions are equal on the opposite sides of the membrane. The colloidal behaviour of proteins is intimately bound up with this unequal distribution of diffusible crystalloidal ions, and the best practical application of Donnan's theory is in the chemistry of tanning.

Jellies or gels constitute a class of colloids which has received extensive investigation, particularly in relation to their structure. Typical jellies are formed by dissolving gelatin or agar-agar in water, and cooling. Various theories of structure have been put forward such as: (*a*) the gel is a more or less rigid emulsion, *i.e.* one liquid dispersed in another liquid; (*b*) the gel is a porous, but continuous, solid cellular framework; (*c*) a liquid phase is enclosed or enmeshed in a honeycomb structure. All these theories fail to account for different phenomena in gels, and the present view inclines to a micellar theory of a gel of a fibrous structure made up of particles or micelles. McBain's work on soap systems gives support to this theory, but further investigation into gel structure is needed.

Solid and Liquid Dispersed in Gas.—Colloidal systems of this type are termed Aerosols. In clouds or fine mists, the disperse phase is liquid; in dust-clouds, metallurgical fumes, or a luminous gas flame, it is solid.

Aerosols present some interesting features not found in other colloidal systems. The small viscosity and density of gases permit more easy separation of the dispersed substance by gravity or centrifugal force. Again, instead of all the dispersed particles possessing electrical charges of the same sign, as would be the case in a liquid or solid medium, some of the particles may be electrically neutral and at the same time others may be charged either positively or negatively.

A mass of valuable theoretical data has been accumulated on the mechanical, optical, electrical, and thermal properties of aerosols, which bears on the general theory of colloids. Space does not permit more than this passing reference.

On the practical side, the subject treats of such important matters as the industrial treatment of smokes and fumes, dust explosions in mines and factories, the smoke nuisance, the combustion of finely-divided liquid and solid fuels, meteorological phenomena (*e.g.* the problem of the dissipation of fog), spray evaporation (*e.g.* the preparation of milk-powder), and smoke in chemical warfare.

The subject of explosions in coal-mines has led to intensive research both at home and abroad. It has been established that $\frac{1}{10}$ oz. of coal dust per cubic foot of air (1 lb. of dust per linear foot

* $p_H = \frac{1}{\log (\text{hydrogen-ion concentration})}$.

of an ordinary mine gangway) will propagate an explosion, *e.g.* due to blasting. The explosion can occur even if the dust-laden air is still or in motion, or is saturated with moisture, and it may reach its maximum at a distance up to 800 feet from its source. Rock-dust barriers, tripped mechanically by the advancing force wave, are used to arrest the propagation of the explosion. From 3 to 4 tons of stone-dust being discharged into the air dilutes the coal-dust in the gangway, stopping the explosion.

The most important industrial advance connected with aerosols is the Lodge-Cottrell method for electrostatically precipitating mists, smokes, and fumes. Briefly, the aerosol is passed through a device with two electrodes (*e.g.* a wire passing down the centre of a long metal pipe), one being negatively charged (the wire) and the other being earthed (the pipe). A voltage of 20,000 to 100,000 volts is employed, giving a potential gradient across the treater pipe of 4,000 to 5,000 volts per cm. The gas is thus ionised, and the dispersed particles become electrically charged, due to the adsorption of ions. Owing to the rapidly alternating polarity of the particles, they clump together to form flakes or drops, as the case may be, and these clumps are heavy enough to settle out provided the gas velocity is sufficiently low (5 to 6 feet per sec.).

In the Great War, smoke clouds were used to conceal the movements of troops, ships, and Zeppelins. An effective smoke-screen was produced by the interaction of zinc dust with carbon tetrachloride in a special mixture, whereby zinc chloride was formed, which was sublimed by the heat of the reaction. Other methods included the ignition of a smoke mixture (made up into " candles " or drums), the detonation of a suitable hygroscopic substance, the chemical interaction of gases such as ammonia and silicon tetrachloride, and by the vaporisation of acid, *e.g.* oleum. Smokes for concealing poison gases, highly dispersed toxic smokes, and coloured signal smokes were also employed, and, without doubt, aerosols will be one of the special features of future warfare.

Liquid Dispersed in Liquid.—When two immiscible liquids are agitated so that one of them becomes dispersed as drops in the other which then acts as a continuous medium, the system is called an Emulsion. Stable concentrated emulsions demand the presence of a third substance, which is called an emulsifying agent, and the function of which is to " protect " the emulsion globules from coalescing. The emulsifying agent is adsorbed at the interface between the drops and the continuous phase, forming a gelatinous, semi-solid, or solid film, depending on the nature of the emulsifying agent used.

With two liquids such as oil and water, two types of emulsion with quite different properties are possible, viz. oil dispersed in water, and water dispersed in oil, and stable emulsions are possible over a range of concentrations up to 99% by volume of the dispersed phase. Water-soluble colloids stabilise emulsions of the oil-in-water type, and oil-soluble colloids the opposite type. Much of the purely scientific development of emulsions has been carried out in England in Donnan's laboratory, whilst the technical development is mainly American, in connection with the " breaking " of crude mineral oil emulsions.

For the production of oil-in-water emulsions, *e.g.* in pharmacy, gelatin, starch, dextrin, gums, and proteins are used. Pickering's classical emulsions of paraffin in water for insecticide sprays were stabilised by soaps, *e.g.* potassium oleate and stearate. He also used finely-divided solids as emulsifying agents, *e.g.* the basic sulphates of iron, copper, nickel, and zinc.

The oil globules in pure oil-in-water emulsions have diameters of the order of 10^{-5} cm., as compared with 10^{-3} cm. for colloidal suspensions, and the globules carry a negative charge. In common with suspensions of fine particles, and colloidal solutions of metals, hydroxides, and

sulphides, fine-grained emulsions show, when examined under the ultra-microscope, that the dispersed particles are in continuous zig-zag motion. The phenomenon, important also in aerosols, is termed the Brownian motion, after the English botanist Brown (1773–1858), who studied the movements of pollen grains in water. It is now agreed that the Brownian motion is due to the bombardment of the dispersed particles by the molecules of the surrounding medium. The motion does not begin in colloidal suspensions or emulsions until the diameters of the particles are reduced to below 3 to 5 μ. The Brownian motion is of particular interest to theoretical chemistry, and has played a most important part in proving the real existence of molecules.

The practical value of the study of emulsions is reflected in the industries dealing with milk, butter, margarine, paints, lubricants, photography, rubber, soaps, mineral oil refining, the production of animal and vegetable oils and fats, ore-flotation, emulsified disinfectants, pharmaceutical emulsions, etc. The subject is of great interest also in physiology, and in this connection Clowes has made extensive investigations into the conditions for the inversion of emulsions, *i.e.* the change over from the oil-in-water type to the water-in-oil type, and *vice versâ*. Apart from its relation to theories of biological systems such as protoplasm, emulsion inversion is familiar in the churning of butter (water-in-oil) from cream (oil-in-water).

The breaking-down of emulsion globules into globules very much smaller, *e.g.* 1/100 the size, is termed homogenisation. Homogenised emulsions are wonderfully stable, *e.g.* homogenised cream will not churn into butter, and cannot be whipped. Such emulsions are used in the preparation of infants' foods, margarine, and ice-cream, of which 300,000,000 gallons were made in the United States of America in 1922.

The de-emulsification of undesirable emulsions such as the crude oil-field emulsions (water-in-oil type), or engine-condensed water, may be accomplished by electrical, chemical, or mechanical methods. The passage of a high potential alternating current as suggested by Cottrell causes coalescence of the water globules. De-emulsification by various electrical methods is now common practice in America. The essential principle of the chemical method is that when an emulsion of water-in-oil is stabilised by an oil-soluble colloid, the addition of a water-soluble colloid can bring about coalescence. Water-soluble soap is usually employed, *e.g.* 0·1 to 1·0% of sodium oleate. Treatment with electrolytes is sometimes favoured, *e.g.* condensed water emulsions (containing small amounts of lubricating oil) may be "broken" by adding aluminium sulphate and caustic soda, the oil-globules uniting with the gelatinous precipitate of aluminium hydroxide. Emulsions may also be separated by the use of centrifugal machines, and, sometimes, by heat treatment, *e.g.* heating crude oil-field emulsions with steam under pressure.

Gas Dispersed in Liquid.—Froth or foam results when a gas is dispersed in a liquid containing some substance capable of being adsorbed at the enormous interface developed, and so acting as a froth-stabiliser. Other conditions for forming foams are of academic interest only. Milk, beer, soap-solutions, and aqueous solutions of many organic substances readily froth. The stabilising substance is usually colloidal, *e.g.* proteins, and Ramsden has shown that the adsorption at the gas/liquid boundary may be so pronounced as to result in a "precipitation" of the colloid, with the formation of a gelatinous, semi-solid, or even solid film.

Froth formation finds great industrial interest in the flotation of ores, and in America alone about 60,000,000 tons of ore are treated in this way each year. To the "pulp" of the crude ore in water is added a small percentage of oil (*e.g.* eucalyptus oil) and the mixture agitated, when the resulting froth is stabilised by the selective adsorption of mineral from the ore. Thus a

mixture of galena and blende with a gangue of quartz, garnet, and rhodonite, as in the ore from the Broken Hill Mine, Australia, under the conditions just mentioned, gives a froth containing mostly galena, a fair amount of gangue, and very little blende. The stable froth is scraped off by suitable apparatus, when, by appropriate flotation principles, further separation of the galena from the gangue is effected.

Another industrial use of froth is found in fire-fighting methods, *e.g.* the Foamite system. Thus a carbon dioxide foam is produced by the interaction of aluminium sulphate and sodium bi-carbonate, the froth being stabilised by colloids such as licorice.

The survey of colloidal systems mentioned in this article is by no means exhaustive. Would space permit, many other phenomena could be treated from the standpoint of colloid chemistry : bread-making, freezing and thawing of meat and fish, the use of boiler-compounds to inhibit scale-formation, adhesives, artificial silk, wood, paper, clays, soils, leather, rubber and vulcanisation, inks, incandescent light filaments, ceramics and hydraulic cements, electrolytic metal deposition, explosives, colloidal fuels, coffee, tea, cocoa, chocolate, mayonnaise, etc. Ostwald has said : " It is simply a fact that colloids constitute the most universal and the commonest of all things we know. We need only to look at the sky, at the earth, or at ourselves to discover colloids or substances closely allied to them. . . . We have only recently come to learn that every structure assumes special properties and a special behaviour when its particles are so small that they can no longer be recognised microscopically, while they are still too large to be called molecules. Only now has the true significance of this region of the colloid dimensions—The World of Neglected Dimensions—become manifest to us."

CATALYSIS

By T. P. Hilditch, D.Sc.

Catalysis is one of the century-old terms which were coined when chemists were veering from phlogistic to atomic ideas, and the foundations of modern atomic chemistry were being laid by Lavoisier, Dalton, Berzelius, Liebig, and the other pioneers of the late eighteenth and early nineteenth centuries.

The name does not, perhaps, show at a glance the nature of the chemical processes which are termed catalytic by the present-day chemist; and so, since of late years this kind of chemical action has been pressed into service to an extraordinary degree in chemical manufacture, and also because catalysis plays a very important part in animal and vegetable life, it is well to illustrate exactly what is meant when a product is said to be made by catalytic action.

If ordinary gaseous ammonia and gaseous hydrochloric acid are allowed to mix together, both gases disappear immediately and a white cloud of solid ammonium chloride or sal-ammoniac is produced; no external agency is required to produce the chemical combination, which proceeds of its own accord.

If we take the elements of hydrochloric acid gas, hydrogen and chlorine, however, and mix these in a similar way, nothing occurs or, at all events, combination is extremely slow. Exposure to bright light or application of sufficient heat (*e.g.* that of an electric spark) causes the production of hydrochloric acid; alternatively, one gas may be (and is in technical practice) burned in the other. In this case a supply of external energy is sufficient to bring about chemical action.

The elementary constituents of ammonia, on the other hand, cannot be brought into union by the application of heat or light alone, and until comparatively recently nitrogen and hydrogen could not be made to combine except in proportions so minute as to be of interest only to abstract science. It was discovered, however, that in presence of suitable chemicals—in this case certain metals—nitrogen and hydrogen united at certain temperatures and degrees of compression and ammonia was formed, not by any means completely, but in sufficient amount to make it a paying proposition to produce the latter gas on a very large scale by this means. The metals used are found to be chemically unchanged when the process is interrupted, and the action is a case of what is known as catalysis. The specific agent employed to bring about the change is known as the catalyst, and the sole common characteristic of this very large class of chemical actions is that the chemical composition of the catalyst concerned is found to be the same at the end of the process as at the beginning.

The actual chemical changes which first focussed attention on this subject included the spontaneous ignition of a mixture of hydrogen and oxygen at the surface of cold spongy platinum, the production of acetic acid from alcohol and air in presence of finely-divided platinum, and other phenomena of a similar nature. As time passed, many other instances were added to those already known and the subject attracted much attention from chemists of all countries, so much so that it may be said to have become one of the best cultivated fields of chemical investigation.

The British workers are not remiss in acknowledging what is owed to chemists of other countries—Sabatier and his co-workers, Haber, Willstätter, or Irving Langmuir amongst many others, but for the moment the object is to emphasise the more recent contributions of British men of science to the industrial applications of catalysis.

As regards the mechanism of catalysis, there are two more or less convergent explanations

at the present day. According to one view, the chemical combination of two substances in presence of a specific third material is due to the condensation of the two former at the surface of the third, resulting in a highly concentrated surface layer of each of the interactants.

Most recently, it has been experimentally proved that these surface layers are only one molecule in thickness, and it is believed by Langmuir, Hardy, and others that the forces which cause the adhesion of the molecular layer are chemical, not physical, in nature.

The alternative view is that catalytic actions are brought about by intermediary chemical combination between the catalytic agent and one or both of the bodies undergoing chemical change; such intermediate compound formation is believed to take place exclusively at the surface of the catalyst and to be in general of a very unstable type. It appears a necessity to upholders of this view that the supposed intermediate compounds should not be too stable, otherwise they would form the final products of change and the catalytic process would come to an end, owing to permanent combination of all the available catalytic agent with one or both of the interactants. In some cases, there is definite proof of intermediate compound formation; in others, there is physico-chemical or purely physical evidence in favour of this view, whilst in other instances the evidence is lacking. One important point may be mentioned which is quoted in favour of a chemical explanation of catalysis, namely, that a given type of chemical action demands as a rule a specific type of catalyst; thus if hydrogen is to be added to or removed from an organic compound, this may often be achieved with the aid of nickel or platinum as a catalyst, but not with alumina or silica, whereas if it is wished to withdraw the elements of water from an organic compound, the latter catalysts are frequently of service, the former never.

For the immediate purpose it is equally interesting to quote Faraday's conclusions on the mechanism of catalysis, deduced ninety years ago, and to observe the relatively small difference in general outlook in spite of the enormously increased detailed knowledge now at our disposal. He is referring specifically to the union of hydrogen and oxygen at a platinum surface: "The only essential condition appears to be a perfectly clean and metallic surface. . . . The gases cannot produce any effect unless the condition of a clean, pure, metallic surface be fulfilled. . . . I am myself prepared to admit (and probably many others are of the same opinion) both with respect to the state of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance."

This sums up, in 1924 as in 1834, both the theory and practice of catalysis. Most of the difficulties and worries connected with technical catalytic processes resolve themselves ultimately into the problem of how to keep the surface of the catalyst clean.

The great attraction, technically speaking, of a catalytic process is that it involves a minimum of waste or undesired by-products together with a more or less complete absence of added chemical reagents. In general, the method is employed in cases where chemical compounds, otherwise inert or requiring added chemicals to effect the desired change, combine or decompose in the desired direction as the result of simple contact with a third substance under appropriate conditions of temperature or pressure.

The most recent developments in industry are mainly examples of what is known as *heterogeneous catalysis:* the catalyst is usually a solid, whilst the interacting materials are either gaseous or liquid.

In contrast to this is *homogeneous catalysis*, in which catalyst and interactants are either all gaseous or all liquid. A familiar example of catalysis in a homogeneous system is the lead-chamber process of sulphuric acid manufacture, where sulphur dioxide and air are converted into sulphur trioxide by means of oxides of nitrogen. Several alternative explanations of the compounds possibly produced before sulphuric acid is finally reached have been given, but essentially the process has been shown to depend on alternate oxidation of nitric oxide to peroxide and reduction of the latter back to nitric oxide. The process is too well known to need further mention other than to point out that it is a typical case of homogeneous gaseous catalysis, with the oxides of nitrogen functioning as catalyst, and that clearly the action proceeds by alternate interaction of the other gases and the catalyst. In practice, of course, some of the oxides of nitrogen pass away from the system, but theoretically one molecule of nitric oxide could cause combination between an infinitely great amount of oxygen and sulphur dioxide.

The formation of organic esters from alcohols and acids in the presence of a small proportion of a mineral acid is another familiar case of homogeneous catalysis, important in the production of perfumes; as a rule, owing to sparing solubility of an ester in its corresponding alcohol the final system is, strictly speaking, heterogeneous and consists of two liquid layers.

Chemists are frequently admonished for inability to write in words which may be understanded of the people, and also for lack of precise definition of the matters under consideration. The etymological purist must be allowed the liberty of his jest in the latter respect, for rigid terminology, however pleasing to the sense, is incorrect when pressed too far in an attempt to separate into gas-tight compartments natural phenomena which overlap and merge into each other without any sharp dividing line.

Catalysis, homogeneous and heterogeneous, is full of cases of this kind, and yet it is very convenient and also necessary to indicate broad distinction in type without committing oneself to too rigid a classification.

It is a disputed point, in fact, whether every chemical action is not in a sense catalytic, and it has been asserted that chemical change between two substances only takes place in presence of some third material. Whilst the writer would prefer not to express an opinion on the point, it may be observed that the example given earlier of a spontaneous chemical interaction (the union of gaseous ammonia and hydrochloric acid) is one case in which it has been proved by the well-known investigations of Dixon and Baker that combination can be inhibited if the gases are perfectly dried before being mixed.

An instance has been given in which a catalytic system, originally homogeneous, becomes a two-phase liquid system as the process nears completion. Reference may next be made to the manufacture of acetaldehyde from acetylene, which has of late years been taken up energetically by the Canadian Electro-Products Company; acetylene is passed into a dilute sulphuric acid solution of mercuric sulphate, when it passes into solution and forms an unstable combination with the dissolved mercury salt which then combines with the elements of water and acetaldehyde is produced.

$$C_2H_2 + H_2O = CH_3{\cdot}CHO.$$

As the process is carried on above the boiling point of aldehyde, the latter is removed continuously in the form of vapour.

The actual catalytic process goes on in a homogeneous solution, but the raw material and product are respectively introduced and removed in the gaseous state.

Again when liquid acetaldehyde is thoroughly mixed with air or oxygen, the latter gas is rapidly absorbed, if the aldehyde is of sufficient purity, and the violently explosive peracetic acid is formed:

$$CH_3{\cdot}CHO + O_2 = CH_3{\cdot}COO{\cdot}OH.$$

If, however, solid manganese acetate is added to the aldehyde before the passage of oxygen is commenced, the peracetic acid at once attacks the manganous salt, which passes into solution as an acetate of a mixture of the higher oxides of manganese; the latter and more aldehyde interact, forming acetic acid and manganous acetate, which decomposes more peracetic acid. This process has often been described as the catalytic oxidation of acetaldehyde by air in presence of manganous acetate, but it is more accurately defined as a method in which the catalytic reduction of peracetic acid by the manganous salt renders the absorption of oxygen by acetaldehyde sufficiently safe to serve as a technical means of synthesising acetic acid from acetylene or alcohol *via* aldehyde. The method was worked extensively in Canada and England, as well as in other countries, during the War period, when the normal supplies of acetic acid from wood-distillation were insufficient to meet the demand.

The processes which are by far the most important of all catalytic phenomena—enzyme action and fermentation—do not fall completely within the scope of a paper dealing mainly with the technical applications of the subject, but are an outstanding example of an apparently homogeneous action which is really heterogeneous. The enzymes themselves operate in a state of colloidal suspension, that is, they are exceedingly finely divided particles of a solid dispersed evenly throughout a liquid medium. This statement refers, of course, to the enzymes themselves; when an action is conducted by means of an organised ferment such as a yeast, the latter is naturally not in colloidal solution in the aqueous medium employed, but the actual chemical changes take place in this case within the cells of the plant wherein the enzymic constituents exist.

Enzymes are extraordinarily specific catalysts, not only in the chemical change they induce (*e.g.* hydrolysis or oxidation), but also in their power of only acting upon compounds of selected molecular constitution and even configuration or shape. They are of fundamental importance in carrying on the normal digestive and respiratory processes of plants and animals, and they are also the most selective and delicate of all known catalysts. They are very sensitive to heat and are usually fatally injured by exposure to temperatures above 50° C., but the fact that they are most active at about 25–35° C. is in itself an inducement to employ them industrially where possible, in order to minimise fuel charges.

Except for such classical examples as the production of alcoholic liquors and of vinegar, however, the technical utilisation of enzymes has not yet attained the importance to which it is entitled. Comparatively recent applications of fermentation to industry are the hydrolysis of fats to fatty acids and glycerine by the enzyme lipase present in castor-oil seeds, the modified fermentation of sugar to produce glycerine instead of alcohol, and the production of acetone and butyl alcohol with hydrogen and carbon dioxide from starch by bacterial fermentation.

In passing, it may be noted that the hydrolysis of fats is frequently carried out by one of two other catalytic processes, known as the autoclave and Twitchell methods. The advantage of such processes over the open soap-pan lies in the replacement of caustic soda for saponification by sodium carbonate for neutralising the fatty acids obtained, in the shorter time in which the

fat is converted to fatty acids, and in the more concentrated glycerine lye which is produced; the colour of the fatty acids and soaps is, however, not always completely satisfactory.

When a neutral fat is heated with water at about 150–160° C. (*i.e.* about 100 lb. per sq. in. steam pressure), hydrolysis proceeds at a relatively slow rate, but in presence of a small percentage of lime or magnesia or zinc oxide (insufficient in amount to combine with all the fatty acid produced) the resolution of the fat into glycerine and fatty acid is complete in a few hours. The action of the mild alkaline base, or of the corresponding soap, is of a catalytic nature.

The Twitchell method depends on the use as hydrolytic agent of a small proportion of a complex sulphonic acid obtained, for example, by condensing naphthalene sulphonic acid with oleic or stearic acid. The mixture of fat and water and Twitchell compound is heated in an open agitator by means of steam, and hydrolysis proceeds steadily.

This process is rather interesting in conjunction with some recent physical theories of catalysis to which reference has already been made. Langmuir and others have established that the layer of a compound concentrated or adsorbed (to use the term most in vogue) at the surface of another is one molecule in thickness, and that this layer is held at the interface by forces which appear to be the same as those which we connote by " chemical affinity." He has also shown that at liquid interfaces the molecules in this layer are not disposed haphazard, but take up an orientated position which is determined by the nature of the groups concerned. Thus in an oleic acid film spread over water, the acid groups are directed towards the water, or perhaps project into the water, whilst the long chain of carbon and hydrogen atoms is displaced away from the water surface.

Now it will be seen that there are two sides to the character of the Twitchell catalyst: the sulphonic acid group will have a strong affinity for water, whilst the stearic or oleic acid part of the compound will be similarly compatible with a neutral fat. Consequently it is particularly adapted to bring about chemical interaction between these two materials, both water and fat becoming associated with the reagent in the first place owing to the presence therein of specifically attractive groups.

This process is also probably a somewhat crude analogy of how the natural enzymes contain specifically disposed compounds, or groups of molecules; but as already stated the mechanism of the structure and resulting activity of enzymes is much more delicate and sensitive than that of any synthetic catalyst so far prepared.

The most notable recent advances in industrial catalysis are those in which chemical combination is effected at the surface of a solid agent, and it is in this domain that Faraday's insistence on the necessity for a " perfectly clean, pure surface " has been proved to be the perfection of sound advice.

A very brief indication of the main industries developed on this basis, especially during the present century, will conclude this article, and it will be seen that chemical processes are carried out by the intervention of a solid catalyst in which either gaseous compounds, liquids, or mixtures of gas and liquid are caused to interact. There are even cases in which reaction proceeds almost in the solid, or at all events the semi-solid state, such as the manufacture of Acheson graphite from coke, which is catalysed by the presence of small quantities of silica or ferric oxide, the carbon first forming a carbide with the other element present (*e.g.* carborundum) and the latter decomposing with production of graphite.

The largest group of modern technical processes based on catalytic action at solid surfaces is that of combination or decomposition of gases.

The contact process of sulphuric acid manufacture is the oldest example, wherein sulphur dioxide and oxygen (air) are caused to combine by passage over heated platinum or heated ferric oxide, instead of by the action of nitrous gases, as in the chamber process. This was patented in 1831 by Phillips, but was not brought to the stage of technical success until Messel took up the study of the process some forty-five years later. The chief obstacle was the "poisoning," or decline in activity, of the platinum catalyst, and this was eventually traced to the presence of arsenic in the sulphur dioxide produced by roasting pyrites. The complete removal of all traces of arsenic was a difficult problem, eventually surmounted; in the course of the work it was found that ferric oxide produced from pyrites was an efficient absorbent for traces of arsenic and also possessed a moderate capacity when heated for inducing the oxidation of sulphur dioxide to trioxide. This led to an improved process wherein about two-thirds of the combination is effected simultaneously with the removal of arsenic by passage over heated iron oxide, the purified mixture being completely converted by passage over heated platinum.

A somewhat similar process of about the same age is the oxidation of ammonia by air at the surface of heated platinum, giving rise to nitric acid, first discovered by Kuhlmann of Alsace in 1830. This method was left unused for even longer than the contact sulphuric acid process, but has been employed on a very large scale during and since the War. The chief difficulties which have had to be overcome in this case are (i) the variety of products which it is possible to obtain (*e.g.* nitrogen), leading to careful proportioning of the air and ammonia in order to obtain complete oxidation, and (ii) the maintenance of a restricted range of temperature. As in the sulphuric acid process, heat is given out during the oxidation of ammonia, and in a modern converter no external heat is supplied once the action has been started, and by means of heat interchangers the gaseous products of the catalysis are caused to give up the excess heat to the incoming mixture of air and ammonia.

This process is in current use by the United Alkali Company, Ltd., both for producing nitric acid and for manufacturing oxides of nitrogen for use in the chamber sulphuric acid process, the old nitre-pots having been eliminated. The catalyst employed is platinum gauze; the activity of a fresh piece of gauze increases to a constant value with use, and the structure of its surface changes, in consonance with the increase in activity, from a smooth to a highly irregular and broken appearance when observed under a microscope.

This is of interest as an indication that the amount of work a catalyst can do is measured by the extent of its effective surface, and it also shows clearly that the platinum has entered into actual combination with the gases.

It is unnecessary to do more than refer briefly to the processes for the synthesis of ammonia from nitrogen and hydrogen, which are based on the pioneer work of Haber and Le Rossignol in 1907; the gases are passed at high pressure (about 100 atmospheres) over a metallic catalyst, usually some form of iron. More recently, Claude has devised apparatus permitting the use of pressures of the order of 1000 atmospheres, with the result that the proportion of ammonia formed by the passage of a given volume of the gases is much higher, since the combination is what is known as equilibrated, *i.e.* the action is never complete, and in this case the higher the pressure the more it proceeds in the direction of ammonia:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 .$$

The use of this process involves the consumption of considerable quantities of hydrogen, and the cost of the hydrogen used forms the greater part of the cost of production of synthetic ammonia.

Unless abundant water power is available for the development of cheap electricity, the most economical method of producing hydrogen on a large scale is from water-gas, produced by passage of steam over coke at about 1000° C., and consisting of about 45 % of hydrogen and carbon monoxide.

When water-gas is passed over heated iron oxide, the latter is reduced to iron, whilst the constituents of the gas are oxidised to carbon dioxide and steam; when steam is passed over the red-hot iron, the reverse action occurs and hydrogen, with iron oxide, is produced. This is one method used in technical practice, and the iron oxide may be said in a sense to act as a catalyst, since it is unchanged by the time the complete cycle of operations has been performed.

In another method, a mixture of water-gas and steam is passed continuously over heated prepared iron or other catalyst, when the carbon monoxide present is converted into carbon dioxide at the expense of the steam :

$$\underset{\text{Water-gas}}{H_2 + CO} + \underset{\text{Steam}}{H_2O} = H_2 + CO_2 + H_2$$

In this process, the large volumes of carbon dioxide formed are removed by scrubbing through water under high pressure.

Other recent proposals to use catalytic methods in connection with gas problems are :

(*a*) In the production of methane (of high calorific value) from water-gas by passage of the latter, with or without steam, over finely-divided nickel :

$$5CO + 5H_2 + H_2O = 2CH_4 + 2H_2 + 3CO_2 \text{ (at 400-500° C., Sabatier).}$$
$$2CO + 2H_2 = CH_4 + CO_2 \text{ (at 250–300° C., Armstrong and Hilditch).}$$

(*b*) In the purification of towns gas from sulphur compounds : Carpenter and the South Metropolitan Gas Company introduced plants about 1914 for the catalytic removal of carbon disulphide and carbon oxysulphide from coal-gas after the free hydrogen sulphide had been removed in the ordinary way. The gas is passed at about 500° C. over nickel deposited on fireclay and the sulphides are converted into hydrogen sulphide and free carbon; the deposit of the latter on the catalyst is removed by periodical exposure to a current of hot air. A plant erected at East Greenwich contained about 12 cwt. of metallic nickel, and was capable of purifying about fifteen million cubic feet of coal-gas per day.

We come, in conclusion, to a number of catalytic processes dealing with the transformation of liquid organic compounds at solid surfaces, the most important being the hydrogenation of unsaturated fatty oils. Sabatier and his co-workers demonstrated that finely-divided nickel has the property, at about 140–200° C., of causing the vapours of many unsaturated organic compounds to take up hydrogen, so that, for example, benzene is converted into *cyclo*hexane, or acetone into isopropyl alcohol, or nitrobenzene into aniline and further into *cyclo*hexylamine by hydrogenation of the aromatic ring system.

Normann first discovered that Sabatier's reaction could be applied to the liquid organic compounds by passing hydrogen through the latter containing nickel in suspension, although it was known somewhat earlier that solutions of organic compounds could be reduced by hydrogen in presence of platinum or palladium when these metals were in colloidal solution.

The technical problem of hydrogenating cheap fatty oils such as whale oil in presence of

nickel, so as to produce fats of semi-solid, tallow-like, or extremely hard consistency, suitable respectively for edible fats, soap-making, or candle manufacture, was worked out between 1903 and 1908, when hardened whale oil commenced to be produced to the extent of about 100–150 tons per week by Messrs. J. Crosfield & Sons at Warrington. The amount of oil hardened at this works rose to about 1000 tons per week during the later stages of the War, and in the meantime other oil-hardening plants had come into operation at Bromborough Port, Selby, and other places, including a large number of Continental and American factories.

The chief difficulties with which the pioneers of oil-hardening were faced were the production of hydrogen economically on a large scale, the preparation of the catalyst in a suitable form for continued use, and the elimination from both the oil and the hydrogen of all impurities which might impair the catalyst surface either by chemical action or by merely clogging or dirtying it by means of a deposited film of inert matter.

Other similar hydrogenation processes which employ nickel but have not yet been widely applied in Britain are the reduction of phenol and the cresols to *cyclo*hexanol and the methyl-*cyclo*hexanols, and the production of the useful solvents tetrahydronaphthalene and decahydronaphthalene by hydrogenation of the naphthalene molecule. It is also possible to reduce many dyestuffs, *e.g.* indigotin, in aqueous solution or suspension to their colourless leuco-compounds.

A certain amount of work has also been carried out on the production of certain pharmaceutical and perfumery chemicals by hydrogenation, but platinum or palladium is more generally employed as catalyst in these cases.

Hydrogen can be removed from alcohols by passing the vapour of the latter over a suitable catalyst at about 300° C., and copper is preferable to nickel as a rule; this process has been used in England for the production of acetaldehyde from alcohol and of camphor from borneol.

In all these cases the first essential is to obtain the specific catalyst which brings about the change in such a form that it presents the largest possible surface for contact with the liquids or gases.

The actual form varies with the conditions. For gas reactions metallic gauze, or the metal or metallic oxide deposited on a very porous but granular inert material as a "support," is usually preferred; occasionally, as in the case of copper, a metal can itself be produced in granules of high porosity.

For reactions in the liquid state where contact is secured by agitation, the catalytic agent is generally deposited on a finely-divided inert support of a very porous and resistant nature.

No attempt has been made to assign any order of relative importance to the foregoing processes, or to give a detailed description of any of the processes mentioned. The object of the article has been to illustrate in as simple a way as possible by reference to selected instances the general nature of the present-day technical practice of catalysis.

THE FATS AND OILS

By John Allan

It might almost be asserted that Fats and Oils are characteristic of the living organism, since they occur throughout the animal and vegetable kingdom in practically all forms of living tissue, simple or complex. Their use as foodstuffs by man must be as old as man himself, though it is probable that their separation in the free state followed only upon the adoption of cooking in the preparation of a meal. The destruction of the cellular tissue in which animal or vegetable fats are enclosed, by heat or pressure, with the consequent liberation of the cell contents, would be an early discovery, and present-day methods of obtaining oils and fats are but modifications of prehistoric processes. So true is this, that a perfect history of the development of the industries concerned with the manufacture of oils and fats might be obtained by collating the various methods of manufacture at present in use throughout the world, beginning with the simple roasting or boiling in water of oil-bearing materials by primitive peoples, up to the advanced methods of autoclave digestion and hydraulic pressing used by the most civilised races. The discovery in very modern times of solvents of a selective character indicated an entirely new method of manufacture and by their aid very large quantities of fats are now separated from the diverse substances with which they are associated in nature.

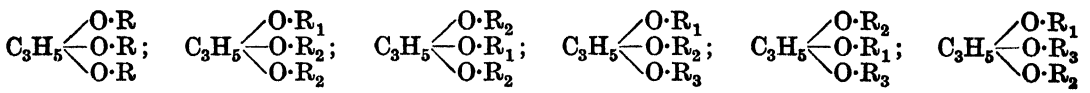
Although historically the preparation of soap must have occurred comparatively late in the period of man's acquaintance with fatty substances, it is an interesting fact that the beginnings of our knowledge of the chemical composition of fats and fatty oils arose from observations made whilst the process known as saponification was being carried out.

Scheele, a Swedish pharmacist, whilst engaged in the manufacture of lead plaster by rubbing together in a mortar olive oil and litharge, observed the separation of a sweet liquid subsequently named glycerine. This was in 1779, but it was left to Chevreul in 1811 to indicate the chemical constitution of the fats by his observation that the manufacture of soap involved the decomposition of a fat into a mixture of fatty acids which combined with the alkali used to effect the decomposition, yielding soap whilst the glycerol was set free. Later Berthelot, by heating fatty acids together with glycerol in sealed tubes, synthesised the fats, thus confirming absolutely the observations of Chevreul. Glycerol is a trihydric alcohol and may combine with one, two, or three radicals of fatty acids, forming mono-, di-, or tri-glycerides. It would appear, however, that in fresh fats only the triglycerides occur. Di- and mono-glycerides have been identified in fats on rare occasions, but always in old and rancid specimens, and it seems certain that these are intermediate products of the hydrolysis of the triglycerides which accompanies pronounced rancidity. Their formation must be accompanied by the liberation of free fatty acids, another characteristic of well-developed rancidity.

The Berthelot synthesis may be expressed thus :

$$C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix} + 3R{\cdot}OH = C_3H_5\begin{matrix}O{\cdot}R\\O{\cdot}R\\O{\cdot}R\end{matrix} + 3H_2O$$

This equation indicates at once that the nature of a triglyceride may be either simple or mixed. The former state is determined by the existence in the glyceride of three fatty acid radicals having the same composition, whilst, in the latter, two only of the acid radicals may be alike, or all three may be dissimilar. A further difference in the nature of mixed glycerides is also possible, since the location of a particular acid radical in the glyceride molecule may also be varied. The composition of these isomeric forms may be indicated thus :



The existence of mixed glycerides in fats has been proved in a large number of cases, and it would appear that many of the properties, and especially the physical characteristics, of fatty substances are due in no small degree to the nature and amount of these substances which are present in them.

Since all the triglycerides of which oils and fats are composed possess in common the glyceryl radical, the variation in chemical properties which they exhibit must be due entirely to differences in the properties of the acid radicals, properties which can readily be ascertained by examination of the fatty acids themselves.

If the glycerides are heated with an aqueous or alcoholic solution of an alkali, saponification ensues, with the formation of glycerol and soap. From the latter, the fatty acids can be set free by treating it with a mineral acid such as hydrochloric or sulphuric acid. The mixture of fatty acids thus obtained is highly complex, but it is generally found to consist in large measure of a few acids the glycerides of which occur in practically all the oils and fats, smaller amounts of many other acids being associated with them. It is a remarkable fact that the acids are entirely monobasic, and generally contain an even number of carbon atoms, and that acids containing an uneven number of carbon atoms are of such rare occurrence that many chemists are not yet prepared to accept their existence as natural glycerides on the evidence that has so far been put forward. Some of the acids belong to the series of which acetic acid is a type, having the general formula $C_nH_{2n+1}\cdot COOH$, and are saturated substances. Their glycerides are the prominent constituents of the solid fats, but they occur in lesser amounts in practically all fatty substances, and in the ordinarily liquid oils their presence is indicated by the separation of solid matter when the oil is allowed to stand for some time, especially at a somewhat reduced temperature. The lower members of the series, especially those containing 10, 12, and 14 carbon atoms, are characteristic of the oils obtained from the kernels contained in the fruits of many palms. Cocoanut oil may be taken as a type of this variety of fat, and the use of this and similar oils in the manufacture of marine soaps is explained by the fact that the soda compounds of the fatty acids of which they are composed are freely soluble in brine solutions, whilst those of acids of higher molecular weight are almost completely insoluble.

Palmitic and stearic acids, which contain 16 and 18 carbon atoms respectively, constitute important members of this series, since, as glycerides, they occur in nearly all fatty substances and are the chief solid constituents of the animal fats and many of those derived from the vegetable kingdom. They are solid substances and the mixture of their glycerides or that of the fatty acids themselves, both of which are technically known as " stearine," is of considerable commercial importance.

An important series of acids, those having the general formula $C_nH_{2n-1}\cdot COOH$, is typified by oleic acid, a liquid at the ordinary temperature, the glyceride of which is the chief constituent of non-drying oils, such as olive, arachis, and the like, and is to be found in greater or less quantity in all oils and fats. The acid is unsaturated to the extent of two hydrogen atoms per molecule, and it slowly absorbs oxygen from the air, with consequent thickening but without absolute drying of its mass. It is the principal constituent of " olein," the liquid substance prepared simultaneously with the solid " stearine " noted above, and is very largely used in the wool industry for various " oiling " purposes.

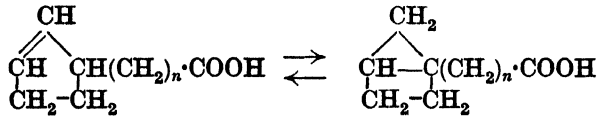
The unsaturated linkage in oleic acid is located between the ninth and tenth carbon atoms and a stereoisomer of the acid known as elaidic acid, a solid body, is formed when oleic acid is treated with nitrous acid or by heating it with sodium bisulphite under pressure. Another solid isomer, *iso*oleic acid, a constituent of that form of commercial " stearine " produced by acid saponification, is also known. These modifications of the acid do not occur in nature as glycerides, but Moore has shown that they are produced during the " hydrogenation " process when oils are treated with hydrogen in presence of catalytic nickel.

Various homologues of oleic acid are known, but none occur in the fatty oils in such quantity as to warrant special description.

The acids of the series having the general formula $C_nH_{2n-3}\cdot COOH$, as typified by the most important member linolic acid, are open chain acids constituted similarly to those of the series we have already considered. They contain two pairs of doubly-linked carbon atoms, a state of unsaturation which has marked effects on the chemical behaviour of the fatty acids and also of their glycerides. The most prominent of the properties thus created is the power they exhibit of absorbing oxygen on exposure to the air with the formation of a varnish-like substance which possesses considerable permanence. As the so-called " drying " oils contain high percentages of the glycerides of this and even more unsaturated acids, their use as paint vehicles and in varnishes is indicated. Investigation of the reactions involved in the drying of oils is hindered by the fact that we have only slight knowledge of the molecular structure of the linolic glycerides —there is evidence that at least two forms occur in linseed oil—but that some form of polymerisation accompanies the oxygen absorption is certain. The variety of linolic acid, variously known as elæomargaric acid and elæostearic acid, which exists as the prominent glyceride of Chinese wood oil is apparently a stereoisomer of one of the linolic acids obtained from linseed oil. Under the influence of heat it polymerises readily to a gelatinous solid and apparently " dries " more rapidly than other linolic acids.

Tariric acid, which occurs as a glyceride in the oil from the seeds of various *Picramnia*, although it has the same general formula as the linolic acids, differs markedly from these in that it contains one triple bond instead of two double bonds. It is the only known case of the occurrence of the triple linkage amongst the fatty oils.

An important departure from the open-chain structure of the linolic acids is found amongst the acids contained in the fat of various *Hydnocarpus* which are of frequent occurrence in India. The acids, which were first fully investigated by Barrowcliff and Power, are cyclic in character, their constitution being expressed by the tautomeric formulæ :



Hydnocarpic acid containing 16 carbon atoms and chaulmoogric acid containing 18 carbon atoms are the only acids of this series which have been examined, but probably other homologues occur. The oils containing them are of particular interest in view of the claims put forward as to their successful use in the treatment of leprosy.

Fatty acids of natural occurrence having the general formula $C_nH_{2n-5}\cdot COOH$ are not numerous, but the glyceride of linolenic acid which contains 18 carbon atoms is an important constituent of the more actively drying vegetable oils. There is some evidence that at least two forms of

the acid occur in linseed oil, but definite proof of this is lacking. If the liquid fatty acids obtained from linseed oil are brominated a crystalline hexabromide melting at 183° C. is obtained. The linolenic acid prepared from this hexabromide by reduction only yields about 23% of the theoretically possible hexabromide on being rebrominated. Rollett suggests the possibility that four brominated compounds can be formed in such a case, and if only one of these is crystalline an explanation is furnished of this apparently anomalous behaviour. Our knowledge of the linolenic acids rests on a highly speculative basis, and much work requires to be done before their properties are defined and the behaviour of their glycerides in the drying oils is understood.

The various fish oils contain a number of highly unsaturated fatty acids belonging to the series $C_nH_{2n-7}\cdot COOH$, of which clupanodonic acid is apparently the most frequently occurring member, as it has been identified in the body, liver, and blubber oils of a large number of marine animals. This acid, which contains 18 carbon atoms, rapidly absorbs oxygen from the air, forming a varnish-like mass. It yields a highly insoluble octobromide which blackens on being heated at 200° C., a property which sharply distinguishes the insoluble bromides of the fish oils from those obtained from vegetable oils.

Still more highly unsaturated acids than this are stated to occur in the fish oils, but their existence is not yet proved. It is probable that the oxidation products of these highly unsaturated acids are responsible for the fishy odour of the oils in which they occur, since the odour of the purified acids is slight, but develops rapidly when they are exposed to the air. The nature of these products is not known, but they can be removed to a considerable extent by refining the oils with caustic soda.

Most of the fatty oils are mixtures of the glycerides of the above-described acids, but the highly characteristic properties of a few oils are due to the fact that they contain a large proportion of hydroxylated acids and in virtue of the hydroxyl group which they contain such acids possess properties common to the alcohols as well as to the acids. The best known acid of this series is ricinoleic acid to which the formula

$$\begin{array}{l} CH_3(CH_2)_5\cdot CH(OH)\cdot CH_2\cdot CH \\ \qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\quad CH(CH_2)_7\cdot COOH \end{array}$$

has been given. Its glyceride is found to the extent of about 90% in castor oil. This fact accounts for many of the highly characteristic properties of the oil, *e.g.* its ready solubility in alcohol and the ease with which it combines with mineral and organic acids to form ester-like compounds, of which the sulphonated product known as Turkey-red oil is the most important. Ricinoleic acid contains an asymmetric carbon atom and is dextrorotatory to polarised light, a property also possessed by its glyceride, so that in a 100 mm. tube castor oil rotates the *D*-ray through 8 to 9 degrees.

Ricinelaidic acid, the stereoisomer of ricinoleic acid, can be obtained in the same way as elaidic acid. It possesses properties parallel to those of the latter with the addition of those conferred upon it by the presence of the hyroxyl group.

Dihydroxystearic acid, a saturated acid containing two hydroxy-groups, is present in castor oil to the extent of about 1%.

Besides the above described acids which, as glycerides, are constituents of the fatty oils, a number of oxidation products of the unsaturated acids are industrially produced. The products of oxidation contain two hydroxy-groups for each double linkage in the molecule, and are usually solid bodies, whereas the unsaturated acids from which they are produced technically are liquids.

Technology

Amongst the greatest of the world's industries, place must certainly be given to those connected with the production and manipulation of oils and fats. It is obviously impossible to present in figures a complete statement of the magnitude of these industries, since their final products are universally prepared and consumed as food or employed as a source of light wherever man exists on the earth. Large quantities of the raw materials of the industry, *i.e.* seeds, nuts, etc., are collected and prepared as " jungle produce," but the proportion of this " wild " product is rapidly lessening before the great increase of the agricultural products raised in the concentrated areas of estates and farms, under the most advanced systems of agricultural control. The most recent example of this is the laying out in Sumatra and Java of extensive plantations of *Elæis guineensis*, the practically self-sown tree the fruits of which yield the palm oil and palm kernels of West African commerce. The plantations are now producing many thousands of tons per annum of oil and kernels under conditions which make them a most formidable competitor in the world's markets. So intensive are the cultural conditions under which the estates are managed that artificial pollination is now carried on over thousands of acres with a resulting increase in yield of almost 100%, and the practice bids fair to revolutionise the production of this and many other oleiferous fruits throughout the tropics.

Excluding butter, linseed oil is probably the most generally used fatty oil in the civilised world, but few of those who handle it have any conception of the enormous areas required to produce the 2½ million tons of seed which are grown in the Argentine, India, the United States, and Canada, the four principal producing countries. The seed yields about 30% of oil or roughly 750,000 tons, 15% of which is used in printing inks and for miscellaneous purposes, whilst the paint, varnish, and linoleum industries consume the remainder.

Little thought also is given to the problems surrounding the transport of this mass of material and to the highly specialised hydraulic plants in which the oil is produced. The development of these plants is largely one of engineering improvements. The primitive method of subdivision by rubbing between stones has given place to trains of heavy steel rollers and other forms of disintegrating machinery, whilst the invention of the hydraulic press by Bramah in 1795, and of the accumulator by Armstrong in 1843, has provided the means of applying the necessary pressure to expel the oil from the subdivided material. The presses at present in use make the expression of oil an intermittent one owing to the alternate nature of the filling and emptying operations. Presses capable of continuous operation have been invented, but their success has been limited to that of the preliminary treatment of highly oleiferous materials, the final expression being effected in a discontinuous type of press.

The extraction of oil by means of solvents is of comparatively recent introduction, since it dates only from 1843, when the large scale manufacture of carbon bisulphide by Jesse Fisher, of Birmingham, made such an operation possible. The development of the process was much hampered by the impure character of the available solvents, and the present-day extension of the process is entirely due to the great improvement in the methods of preparing and refining petroleum spirit, the solvent now most generally employed. Formerly applied to low grade and waste materials only, the process is now used in the production of both oils and cattle foods of the highest quality. Various chlorinated hydrocarbons, such as carbon tetrachloride, trichloroethylene, tetrachloroethane, etc., have been recently suggested as solvents, but for various reasons their application has been particular rather than general.

Present-day preparation of the animal fats exhibits nothing more than plant development of what must have been the pre-historic process of heating fatty tissue in water and skimming off the fat as it was liberated.

The fat of sheep, cattle, pigs, marine mammals, and fish, and various waste animal products, are all subjected to this process of " rendering." The small open pan in which the operation was formerly carried out has, however, given place to large, vertical, boiler-like vessels working under pressure, many of which have a capacity of 20 tons. The yield of fat thus obtained is greater than by the older method, and the non-fatty residue is in a highly suitable condition for use as a nitrogenous manure. The equipment of large steamers with rendering plant of this type is an interesting recent development of the whaling industry. Various processes of low temperature " rendering " are also employed for the preparation of high grade edible products, and with the continued increase in the demand for such fats which are used in the manufacture of margarine and lard compound, the pressure process is being more than ever applied to non-edible and low-grade materials.

It is difficult to realise that it is only fifty years since Mege-Mouries, under the stimulus of a prize offered by the French Government, first prepared margarine. Its use as a foodstuff was at first small, but to-day it may be said that it is one of the staple fatty-foods of the world. This development has only become possible by the great progress which has been made in refining and deodorising oils. Present-day refining involves the complete removal of free fatty acids from the oil, which is done by treatment with alkalis, preceded or followed by a decolorising process in which such materials as fuller's earth, charcoal, and the like are employed. Oils thus preliminarily treated are deodorised by passing a current of steam through them at temperatures which vary from 150–200° C., a high vacuum being maintained in the vessel throughout the four to ten hours which the process occupies. Practically all the known oils can be rendered free from odour by this process, but the permanence of this condition is not always assured. It would appear that this reversion is associated with the existence in the deodorised oil of glycerides of highly unsaturated acids, since oils which contain these glycerides in small amount only are relatively more permanent.

The behaviour of the drying oils on exposure to the air and the very great increase in the rapidity of drying which is brought about by " boiling " the oil has been the basis of much investigation, but the nature of the " boiled " oil and the mechanism of " drying " is not yet understood.

The boiling process consists in heating the oil to about 150° C. for a varying number of hours, according to the type of boiled oil which it is desired to prepare, in contact with a small amount of substances called " driers." These " driers " are salts of lead, manganese or cobalt, and whereas formerly the oxides of the metals were almost exclusively used, in present-day practice such salts as the resinates and linoleates are much more largely employed. These new driers are not pure compounds, but are the substances obtained when the water soluble soda soaps of ordinary colophany or linseed oil are treated with water soluble salts of the particular drier it is intended to prepare.

It has been generally accepted that the increased rate of absorption which results from the presence of driers is largely a catalytic acceleration of the drying of the raw oil. When raw linseed oil is exposed to the air, it is found to dry in two stages, an induction period which covers a considerable portion of the total time of oxygen absorption ending with a rapid gelatinisation of the oil, which is the beginning of the final oxidation period. When oil, boiled in presence of

driers, is exposed, the induction period is practically non-existent and drying apparently goes on from the point at which gelatinisation sets in with the raw oil. Until it has been proved that the final products of the two types of drying are identical, it cannot be assumed that the course of oxidation of the two classes of oil is similar.

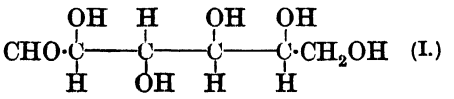
As a result of the higher market value of the solid fats and the demand created by the use of solid fatty acids in the form of stearine for candle manufacture, the conversion of liquid oils into solids has long been the basis of much experimental work. Since the commonly occurring solid fatty acids are saturated substances whilst the liquid fatty acids are unsaturated to a varying extent, it was early evident that solid fatty acids or their glycerides would be obtained if saturation of the liquid acids could be effected. If oleic acid be heated with fuming hydriodic acid and amorphous phosphorus for several hours at 200° C., stearic acid is obtained, as also is the case when oleic acid is heated with 1% of iodine at 270–280° C. For obvious reasons, neither of these processes could be economically successful. The preparation of palmitic acid by fusing oleic acid with an excess of caustic alkali (Varrentrapp's reaction) has been tried on the large scale, but was not commercially practicable. The classical work of Sabatier and Senderens on the saturation of various organic substances by means of hydrogen in presence of catalytic metals provided the means of solving the problem. Attempts to hydrogenate oleic acid in vapour form in presence of a nickel catalyst were partly successful, but the discovery by Normann that the unsaturated glycerides could be hydrogenated by passing hydrogen through them in presence of catalytic nickel at temperatures below that at which they volatilise brought the production of solid into liquid fats within the bounds of commercial possibility. Normann's patent dated from January, 1903, and it has been followed by an extraordinary number of patents for apparatus in which to carry out the hydrogenating process. The commercial effects of the application of the process are interesting in that its unqualified success has now brought with it limitations, and the formerly cheap liquid oils have advanced so much in price that in very many cases it is no longer economical to hydrogenate them. The developments of the process following upon Normann's discovery were largely concerned with plant either for the preparation of the catalyst or the actual hydrogenating operation. Further study of the catalyst and preliminary treatment of the oil have so advanced the manipulation, however, that the hydrogenation can be carried out in almost any form of vessel with only a minimum of agitation.

The production of cheap hydrogen and the development of a satisfactory continuous process are the keys to the next advance, for undoubtedly, so far as plant and catalyst are concerned, the difficulties of the intermittent plant have been overcome.

THE SUGARS AND CARBOHYDRATES

By J. C. Irvine, LL.D., F.R.S.

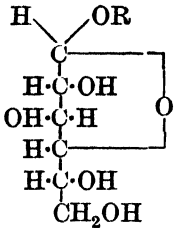
From whichever standpoint they may be viewed—chemical, biological or physiological—the sugars and allied carbohydrates must be recognised as occupying a position of unique importance among natural products. The exact scientific study of these compounds is, however, surrounded by many difficulties, and a comparison of the position reached to-day with that attained at the beginning of the century shows that in no branch of organic chemistry more than in carbohydrates is progress dependent on the development of theories of structure. The end of the nineteenth century closed the brilliant period of Fischer's researches which provided chemists with new facilities for expressing the reactions of sugars in terms of structure and of configuration. In consequence, research in this field has since become less descriptive and has focussed largely on the constitutional exploration of sugar molecules. The part played by British investigators in the advancement of this fundamental aspect of carbohydrate chemistry is of great importance and has had far-reaching results, not alone in chemistry but also in the related sciences. It is necessary to trace the steps which have led up to this development, and attention may in the first place be directed to some theoretical considerations affecting the constitution of the simple monosaccharides, of which glucose may be taken as a type. Twenty-five years ago, the formula for glucose in general use was that of a pentahydroxyaldehyde, the configuration of which is represented by the expression shown below :



(I.)

This view was held with great persistence and was challenged only after it was recognised that comparatively few reactions of glucose could be ascribed to the presence of an unmodified aldehydic group. Further, it became clear that although in the glucose molecule there are five hydroxyl groups, one of these groups possesses properties which show that it is associated with the part of the molecule responsible for the reducing action. The conversion of glucose into methylglucoside may be cited in illustration. It is doubtful if a satisfactory explanation of such reactions could have been provided by chemical methods alone, and an improved formula for the sugar was arrived at through the study of the phenomenon known as mutarotation. This expression is applied to the alteration in rotatory power exhibited when glucose or other reducing sugar is dissolved in water, and, from time to time, many explanations have been put forward to account for the change. The original view that the permanent formation of a hydrate takes place soon became untenable and Lowry's observation that nitro-camphor shows mutarotation in non-aqueous solvents indicated that reversible isomeric change is the responsible agent. It was therefore suggested that each reducing sugar can exist in two isomeric forms which, on solution, undergo interconversion, giving an equilibrium mixture of the isomerides. Two forms of glucose were actually known at the time, viz. α-glucose showing $[\alpha]_D + 106° \longrightarrow + 53°$, and β-glucose, which displays the reverse change $[\alpha]_D + 22° \longrightarrow + 53°$. Taken in conjunction with the formula assigned to the isomeric methylglucosides, this theory of mutarotation was applied so as to formulate the two principal isomeric varieties of glucose. Further, by the ingenious method of hydrolysing each methylglucoside by the appropriate enzyme, and thereafter ascertaining the direction of mutarotation exhibited by the liberated sugars, it was shown by E. F. Armstrong that α- and β-glucose are the lower homologues of α- and β-methylglucosides. The combined

results of these investigations indicated the following formula for the glucoses or their glucosidic derivatives, and have proved of general application.



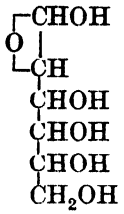
where R = Hydrogen or a Substituting Group, and OR may be placed to right or left of the configuration diagram. (II.)

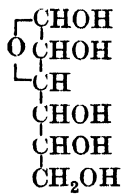
The acceptance of this formula has opened up other problems as, for example, the allocation of a definite position to the reducing hydroxyl group in α- and β-glucose respectively, the mechanism of mutarotation, the specific reactions of the individual hydroxyl groups, and confirmation of the position assigned to the internal oxygen ring. In the case of glucose, the first of these factors has been supplied by Böeseken on the basis of physical measurements conducted on solutions of the sugar in the presence of boric acid. With regard to the mechanism of mutarotation, several alternatives have been suggested. If the change proceeds through an intermediate form, this may either be the aldehyde or its hydrate (Lowry). Experimental evidence has been obtained that, in the presence of water, an oxonium hydrate containing the group $\overset{H}{HO}\!>\!O\!<$ is formed from glucose, and mutarotation can be explained by postulating the alternate formation and decomposition of this compound (E. F. Armstrong; Irvine and Steele). Irvine and his pupils have shown, however, that the mutarotation of methylated sugars may take place in non-aqueous solvents, and that, in certain cases, the change may be entirely suspended until promoted by a catalyst. The subject is therefore full of complications, and it seems unlikely that any single explanation will cover all cases.

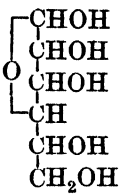
Consideration of the optical activity displayed by sugars necessitates reference to a number of important principles established by Hudson and his colleagues. In general, it has been shown that the molecular specific rotation of a sugar (or its derivatives) depends on two numerical factors, one contributed by the terminal asymmetric system, and the other by the remainder of the molecule. Representing these factors by a and b, the molecular rotation of an α-form will be $+ a + b$, and that of the β-isomeride $- a + b$. The magnitude of a and b can be ascertained and thus exact initial rotation values may be calculated so that an appropriate configuration can be assigned to any compound existing in two mutarotatory forms (Irvine and Hogg). It is impossible within the limits of space available to do justice to the importance of this work, but an immediate practical advantage conferred on sugar chemistry by the American school is the refinement introduced into the working methods for obtaining pure stereochemical varieties of sugars.

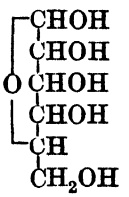
For a space of fifteen years the butylene-oxide formula for glucose held undisputed sway, but Emil Fischer's and Irvine, Fyfe, and Hogg's observations that more than two forms of methyl-glucoside exist created a new situation. By the use of experimental methods developed by the School of Chemistry at St. Andrews, these new glucosides have been shown to be derived from a variety of glucose, termed provisionally "γ-glucose," which differs from the normal type in the position occupied by the internal oxygen ring. The same complication is probably general,

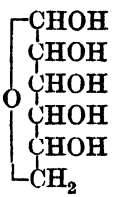
having been encountered in fructose, galactose, mannose and other reducing sugars. In consequence, it can no longer be assumed that the butylene-oxide structure is applicable to all reducing sugars in all circumstances. Selecting an aldo-hexose in illustration, any of the following types may exist, either independently or side by side :


(III.)


(IV.)


(V.)

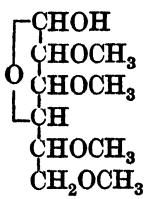

(VI.)

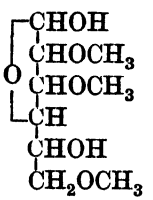

(VII.)

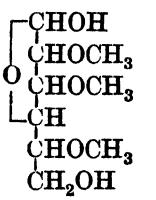
This fundamental generalisation has been arrived at and many other constitutional problems of carbohydrate chemistry have been solved through the study of methylated sugars, to which reference is now made.

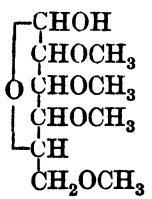
Methylated Sugars and their Applications

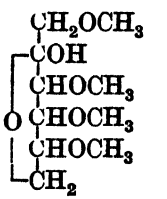
Although hydrolysis can corrupt a glucoside, a disaccharide, or a polysaccharide into sugars which may be identified, the union of the components is not revealed and the position of the oxygen linkage in the sugar remains uncertain. This has hitherto been an insuperable obstacle in solving the structure of complex sugar derivatives, but in the period under review, a notable advance, due to the work of the St. Andrews laboratories, has been made in extending the scope of such inquiries. A sugar, or equally a compound containing sugar residues, can be methylated so as to replace the free hydroxyl groups by stable methoxyl groups. These survive hydrolysis, and consequently, in the cleavage products obtained from the methylated derivative, methyl groups are attached in the positions not involved in the union of the components. A summary of the progress made up to 1923 by the application of this principle has been given in a lecture delivered by the writer to the Chemical Society of London, and in an address to the Chemistry Section of the British Association in 1922. Reference to these publications and to the original papers will show that the methylation method is of general application in solving constitution and that a large variety of completely and partly methylated carbohydrates of all types has been examined. These compounds are extremely suitable for exact experimental study, and can be identified with certainty, even when only small quantities are available. Out of forty examples of simple methylated aldoses and ketoses, the following have proved of greatest service in determining the constitution of glucosides, disaccharides, and polysaccharides :


2 : 3 : 5 : 6-Tetramethyl glucose.
(VIII.)


2 : 3 : 6-Trimethyl glucose.
(IX.)

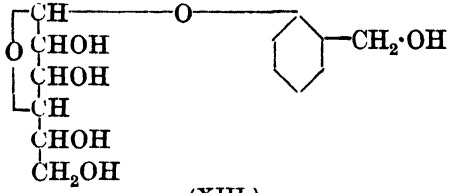

2 : 3 : 5-Trimethyl glucose.
(X.)


2 : 3 : 4 : 6-Tetramethyl galactose.
(XI.)


Tetramethyl γ-fructose.
(XII.)

It will be observed that the necessity to discriminate between isomeric methylated sugars has led to the adoption in the literature of a numerical system of nomenclature in this group.

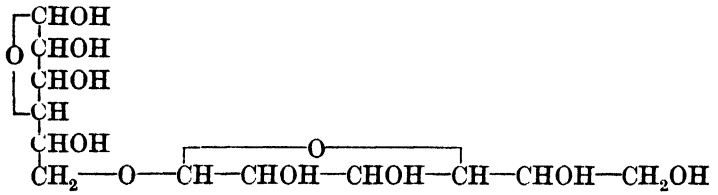
The application of the scheme outlined above may be illustrated by reference to the case of salicin. This glucoside gives a pentamethyl derivative which, on hydrolysis, yields, as ultimate products, 2 : 3 : 5 : 6-tetramethyl glucose together with saligenin methyl ether. From this result, the structure of the parent glucoside is at once revealed to be :



(XIII.)

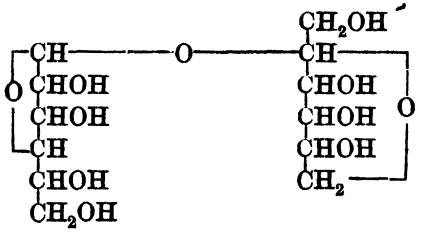
Precisely similar principles apply to the constitutional studies carried out on indican, arbutin, amygdalin and other natural or synthetic glucosides (Macbeth, Haworth).

Turning to the parallel case of disaccharides, the results obtained with maltose may be quoted as typical of many others which have been obtained by the St. Andrews school. A fully methylated maltose gave on hydrolysis an equimolecular mixture of the methylated glucoses formulated as VIII and X. From this it follows that maltose has the structure :



and, by precisely similar methods, the essential structure of other reducing disaccharides has been established (Haworth).

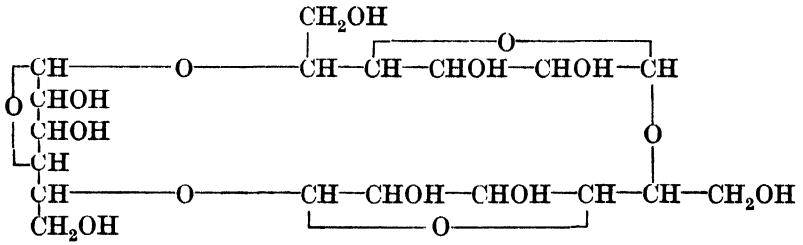
The important case of sucrose deserves special mention, as it illustrates how hydrolysis of an unsubstituted sugar may give a misleading result. It has long been known that octamethyl sucrose yields 2 : 3 : 5 : 6-tetramethyl glucose as one product and the other sugar has now been recognised as a derivative of the amylene-oxide form of fructose. According to this view, the formula for sucrose becomes :



Evidently the fructose residue present in sucrose has a different constitution from that of the normal ketose, and provisionally the name " γ-fructose " has been assigned to it. The expression

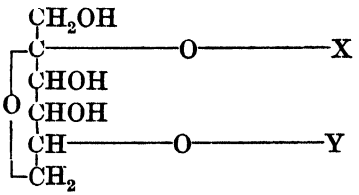
" γ-sugar " is, in fact, used generally to include all forms of a sugar in which the oxygen ring is displaced from the normal stable position, and the recognition of these isomerides, attributable solely to the efforts of British chemists, not only opens out a wide range of future work but necessitates a review of past work in a new light.

For obvious reasons the exact chemical study of the polysaccharides is beset with so many difficulties that, until recently, ideas as to constitution were vague and largely speculative. The study of methylated glucosides and simple saccharides was conducted primarily with the object of collecting the information necessary to explore this field and render intelligible the essential reactions of more complex saccharides. As the chemistry of cellulose is dealt with in another section of this volume, reference is now restricted to researches designed to characterise the molecular unit of the polysaccharide. Cotton cellulose, when subjected to the methylation process followed by hydrolysis, gave a quantitative yield of 2 : 3 : 6-trimethyl glucose. From this result it follows that the older constitutional formulæ ascribed to cellulose must be discarded, and good reasons exist for the claim that this polysaccharide consists of the unit shown below, polymerised in unknown numbers.



The chemistry of starch is a subject long associated with British enterprise and research. The survey of natural processes in which starch is formed, the action of enzymes on the polysaccharide, and the dissection of starch into its components are all subjects which, throughout the second half of the nineteenth century, were prominent in publications emanating from British sources. To the progress already made has now to be added the further advance that one component of starch behaves similarly to cellulose and gives rise to the same form of trimethyl glucose.

Through the properties of its methyl derivatives, the constitution of glycogen has also been investigated, and special reference may be made to the unique case of inulin (Irvine and Steele). This polysaccharide stands alone in that it is composed entirely of anhydro-γ-fructose residues, substituted as shown below :



These examples will suffice to show the value of the methylation process, but they do not exhaust the uses of methylated sugars either in solving constitution or in tracing the mechanism of reactions in which sugars play a part.

General Reactions of the Sugars

Having traced the principal researches which have led to current views on structure, a survey may now be given of other experimental advances made since the opening of the century. For simplicity, the various problems are discussed under appropriate headings.

Synthesis of Sugars.—It is interesting to note that the efforts of British investigators, extending over 150 years, now embrace the complete range of carbohydrate chemistry from formaldehyde at the one extreme to cellulose and starch at the other. The initiation of research on the natural synthesis of carbohydrates may be accredited to Joseph Priestley, who, so long ago as 1771, showed that carbon dioxide is necessary for assimilation. The subsequent work of Brown and Morris and of Usher and Priestley form the connecting links with the attempts now being made to elaborate sugars from simple compounds by the auto-condensation of formaldehyde under the influence of light of selected wave-length. This investigation, which is associated with the University of Liverpool, employs an entirely new line of attack, and aims at reproducing the physical conditions which function in natural photosynthesis.

Glucosides.—Probably the most important discovery under this heading is the recognition that a sugar may form more than one pair of isomeric glucosides differing in the position of the oxygen ring. Researches which have as their object the synthesis of the normal stable types of glucosides have been largely confined to the use of tetra-acetyl-bromoglucose or analogous compounds. These reagents have been employed with marked success both in this country and abroad, and reference need be made only to such outstanding examples as the glucosides derived from cholesterol and the related alcohols or from hydroxy-terpenes. Glucosides of an entirely new type, which indicate a relationship between amino-sugars and the betaines, are also available, as Irvine has shown that a series of amino-glucosides can be prepared from *d*-glucosamine. At the same time, the study of natural glucosides has not been overlooked, and the work of A. G. Perkin and Everest on glucosides associated with plant pigments may be cited to show that research in this difficult field has been actively prosecuted, although the brilliant investigations of Willstätter have not yet reached a stage which brings them within the scope of structural carbohydrate chemistry. In addition, special attention has been directed by H. E. and E. F. Armstrong and Horton to natural nitrogenous glucosides, particularly with regard to their occurrence and the mechanism whereby they are hydrolysed, issues of the widest importance to the economic botanist.

Acyl Derivatives.—In this particular section, research activity may be traced to the efforts made by Fischer to synthesise compounds related to the tannins, and this has led to a revival of interest in sugar derivatives of the type

$$CH_2OR{\cdot}CHOR{\cdot}\underbrace{CH{\cdot}CHOR{\cdot}CHOR{\cdot}CHOR}_{O}$$

where R = an acyl residue of high molecular weight. In addition, various synthetic fats, such as pentastearyl glucose, have been prepared, and these compounds are constituted on the above structural model although they are not the only representatives of synthetic carbohydrate fats now known.

Oxidation and Reduction of Sugars.—Although no improved methods of oxidising sugars have recently been described, the earlier work of Fenton in this connection has proved of permanent service. For example, the degradation of aldoses by Ruff's process depends essentially upon the

use of hydrogen peroxide, which possesses an enormous advantage over bromine in that disturbance of constitution is less likely to take place.

Turning to the converse problem of reduction, the older methods have been so much improved that during the War it was possible to prepare at St. Andrews the large quantities of dulcitol and other polyhydric alcohols which were required for the use of bacteriologists. This enlargement of laboratory methods to manufacturing requirements is, of necessity, based upon much exploratory research on the condition assumed by sugars in alkaline and acid media.

Alcohols Related to the Sugars.—A superficial view might lead to the conclusion that the polyhydric alcohols have been so thoroughly examined that little opportunity remains for further research on these compounds. This is not the case, however, as the study of such a familiar compound as mannitol has revealed that each individual hydroxyl group possesses its own specific reactions and that the hydroxyl groups at opposite ends of the carbon chain show entirely different properties. This demands a modified formula for the compound, and the point is important, particularly in view of the physiological issues which are concerned. Similar enquiries conducted on dulcitol occupied Fischer in the closing years of his life, and a striking example of the necessity to study separately each hydroxyl position of a sugar is shown by the results obtained in the pioneer work of Macleod and Herring in tracing the effect of different sugars as antidotes to insulin. Once again the ultimate importance of structural study becomes apparent.

Condensation Derivatives of Sugars.—Recognition of γ-sugars has led to a revival of interest in sugar derivatives which resemble γ glucosides in the ease with which they are hydrolysed. Of such compounds the most important are the *iso*propylidene derivatives obtained by condensing a sugar with acetone. Much laborious investigation has been devoted to these derivatives in this country, in America, and on the Continent, and although, so far, no dramatic discovery is associated with this work, it has been of the utmost value in revealing unexpected complications in sugar reactions.

It is somewhat remarkable that attempts to promote the auto-condensation of sugars by the agency of acids have met with comparatively little success, and this is probably due in large measure to the fact that acids induce intramolecular dehydration in several parts of the molecule. From the experimental point of view, a narrow line divides a reaction such as the formation of an *iso*maltose from glucose and the complete disruption of the hexose to give ketonic acids. Before leaving the subject of the action of acids on carbohydrates, the important reaction developed by Fenton may be recalled. Hydrogen bromide under suitable conditions acts on keto-hexoses to give bromo-methylfurfural, which is formed in varying amount according to the nature of the hexose employed. This reaction can be utilised as a very delicate test for hexoses, and plays an important part in studying the polyoses which are related to the hexoses.

Amino-derivatives of Sugars.—*d*-Glucosamine continues to remain the member of this class which has received most attention, and the compound still provides many complicated problems. The relationship of the amino-sugar to the hexoses is still an open question, as although glucosamine has been transformed into glucose it has also been converted into mannose. Extremely important work carried out by Levene and his school certainly points to the mannose configuration as the more probable, but the application of Hudson's Rule to the compound leads to the opposite conclusion. Research on a related problem has confirmed that by the action of ammonia and alkylamines on reducing sugars the first definite product is the corresponding imino-glucoside, and the same type of condensation occurs when amino-acids react with sugars.

It is somewhat surprising to find that this important branch of research has not attracted many workers, but it is reassuring that a large share of the progress made is attributable to researches proceeding from this country.

Action of Enzymes.—The scientific study of enzyme action, including fermentation, has always been actively pursued in British schools of research. The work of Brown, O'Sullivan, and Croft Hill, although belonging to an earlier period than that now under review, laid the foundation for much of the most important research in this field. Curiously enough, the application of enzyme action to synthesis, foreshadowed by Croft Hill, has been developed almost exclusively in France, where the collaboration of Bourquelot, Aubry, and Bridel presents a notable achievement. The biochemical syntheses effected by enzyme action bear a striking similarity to those of natural processes and constitute an entirely new chapter in sugar chemistry. In addition, enzymes are now used as distinctive reagents for identifying the linkage of one sugar residue with another, for relegating glucosides to their class, and for effecting the analytical separation of sugars.

The study of fermentation attracts many workers, and so many complications have been revealed that great divergence of opinion exists as to the mechanism of the reactions involved. The stimulus conveyed by Buchner's papers on the action of zymase has led to a systematic scientific study of the numerous factors involved in fermentation and has opened up many problems of interest to the sugar chemist. Amongst these may be mentioned the biochemical investigation of a hexose diphosphate and of two isomeric hexose monophosphates, compounds which are obtained either directly or indirectly by the action of yeasts on glucose, mannose or fructose in the presence of phosphates. Their detailed study, which is identified particularly with the work of the Lister Institute, represents a branch of research full of possibilities. Before leaving the subject of enzymes, reference should be made to a practical application of enzyme action which has a bearing on the constitution of starch, and, in association with other work, may be developed on profitable lines. Methods of dissecting the " starches " into their main constituents present many practical difficulties, but by the use of special diastase the amylose and amylopectin components can be separated accurately. In this way it has been shown by Ling and Nanji that whilst the amylose fraction of starch yields maltose quantitatively, the amylopectin is convertible into a trisaccharide. The latter in turn may be hydrolysed to give either maltose or *iso*maltose, so that the whole question of the transformation of starch into disaccharides must now be viewed in a new light.

The foregoing synopsis does not represent research in all branches of carbohydrates, but is intended to give in general perspective a view of the activities of the past twenty-five years which are most likely to influence the progress to be expected in the ensuing quarter of a century. A fair estimate of the present position leads to the opinion that this branch of chemical enquiry is passing through a period of unusual activity and that this country has reason to be satisfied with the part played by its scientific workers in a development of wide importance affecting many aspects of human activity.

CELLULOSE

By C. F. Cross, F.R.S.

Cellulose is not a creation of Science in the sense in which benzene may be so described: the investigations of "cellulose" have resulted in an enormous accumulation of data, of the order of exact knowledge in the scientific sense, but have not contributed any primary development of the fundamental grammar of the natural sciences; whereas the literature of benzene chemistry shows that, in an important phase, the development of organic chemistry was almost co-extensive with the contributions from the intensive investigation of the "aromatic" series of carbon compounds. Further, although the latter was powerfully stimulated by correlative industrial applications of its products, the objective was pure science, and the commercial developments were of the incidental, sometimes accidental, order.

In the "cellulose" arena, on the other hand, the basis of investigation was empirical, and if in our age these investigations have established a definite chapter in our encyclopædia of the knowledge of Matter, it still lacks the characteristics of those sections of the Book of Science which owe nothing to Industry and little more to the empiric.

The story of the scientific-technical progress which has resulted may not commend itself to the modern chemist as "Biblical." It certainly could not be adequately told after the model of "Beilstein." But he would recognise the philosophical basis of divergence in the significant facts: (1) that we are still ignorant of the fundamental constitution of cellulose; (2) we are ignorant of the relationship of constitution to organic structural form, and (3) we study cellulose through an infinity of processes of degradation (of the complex), but are unable to control any up-grade process of change.

One other consideration of primary importance: the cellulose raw material of our industries is mostly exotic. In Great Britain we produce a portion of the flax required for the linen industry, and a fractional proportion of the wood required for building construction and other uses. Within the Empire, it is true, we produce a notable quantity of cotton and a large proportion of the world's consumption of jute. But in regard to scientific technical development the workers of the British Islands have been concerned with "cellulose" as an exotic supply.

We use the term "cellulose" as the comprehensive expression for the non-nitrogenous basis of the vegetable world. Plant structures are variable through infinite gradations of form as of substance, but present equally characteristic features of typical uniformity whether as organised structures, cells, fibres (elongated cells), tissues, or as organic (carbon) compounds of well-defined composition and constitution.

The structural characteristics and properties of "cellulose" are the basis of most important industries in which they are not merely utilised, but very considerably developed. These industries are industrial Arts, and contribute largely to the æsthetic development of individuals and nations. The more important are:

Textile. Production of fabrics from

Fine textiles. (*a*) Cotton, flax, hemp, ramie. Mainly clothing and dress materials.

Coarse textiles. (*b*) Jute and low grade forms of (*a*). Mainly wrapping, baling and covering materials.

(*c*) Manila, sizal, phormium and lower grades of (*a*). Twine, rope and cordage.

Miscellaneous fabrics. (*d*) Cereal straws and wood. Raffia, hat-making.
(*e*) Miscellaneous fibres and tissues, *e.g.* coconut (coir) bast, kapok. Mat-making, upholstery stuffing, etc.

PAPER MAKING. Production of papers, boards, pressure moulded pulp articles, twisted paper, yarns, from
All the above, mainly as wastes and industrial rejecta
and
Pulps from woods and esparto.

BUILDING CONSTRUCTION / FURNITURE IMPLEMENTS } Wood structures (timber) fashioned by carpenter, joiner, turner.

These industries and arts have been evolved from primitive forms; their later developments involve exact knowledge and the methods of science; but the characteristics of development are rather those of empiricism and craftsmanship, and they are not to be treated as a section of " science " in the exclusive sense of the term.

In the natural world there is an organic cycle, Life—Decay and Death—Life, in accordance with which plant structures are broken down to be reassimilated. The more resistant components constitute the *humus* of soils, and in massive aggregates *peat* and the *lignite-coal* series of graduated density and carbon concentration.

These are only mentioned to complete the picture of cellulose and to emphasise its predominant importance.

We use the term Cellulose as denoting a chemical type. The individual celluloses are compounds of great stability in relation to oxygen and water and the conditions of our planet; and are characterised by general non-reactivity and resistance to the severe treatments required for their isolation and purification incidental to the paper-making and textile industries. Such treatments, of alkaline digestion (caustic alkalis at high temperatures) and oxidation (bleaching by hypochlorites), resolve the natural celluloses which are compounds or mixed complexes of

Cellulose and Pectin.	*Cellulose and Lignone.*	*Cellulose and Fatty Acids.*
Cotton, flax, ramie.	Jute and wood structures	Cuticular tissue, cork structures.

In the ultimate separation of cellulose, more or less chemically pure, the fibrous structure and characteristics are fully maintained. The cellulose, as *pulp* or *half-stuff*, is the fibrous raw material of the *paper-making* industry; mechanically prepared and treated, the discontinuous fibres or fibre-fractions are converted into a continuous web or fabric which is paper (cellulose papers).

Papers are also made from the compound or mixed cellulose, *i.e.* the natural " celluloses," receiving only mechanical treatment to produce a uniform disintegrated fibre-pulp and the conditions necessary for suspending in water and carrying on the continuous wire of the paper machine.

Cellulose, however, is reactive through its hydroxyl groups, to be converted into derivative forms in which the essential physical properties of the complex are maintained—but with the added or developed characteristics of a soluble or plastic colloid, which conditions industrial developments of great magnitude; thus:

ANHYDRO-ESTERS.—*Cellulose nitrates* or "nitrocelluloses," by reaction with nitric acid. Industrial applications: Explosives, celluloid and collodion, artificial silk (denitrated to cellulose).

Cellulose acetates, by reaction with acetic acid (anhydride). Industrial applications: Waterproofing dopes, artificial silk (as cellulose ester).

HYDRATE ESTERS.—*Cellulose xanthogenic acids*, by reaction with caustic soda and carbon disulphide. Industrial applications: Films, artificial silk, threads and ribands.

COLLOIDAL HYDRATE COMPOUNDS.—*Cellulose Cuprammonium*, interaction of groups resulting in solution of the cellulose. Industrial applications: Waterproofing, textiles, artificial silk and threads.

Cellulose zinc chloride, interaction of groups resulting in solution. Industrial applications: "Vulcanised" fibre products.

These derivative compounds with their industrial applications are of great importance; they represent developments of the colloid-structural qualities and capabilities of the natural products or forms of cellulose.

CELLULOSE AND CAUSTIC SODA.—*Alkali-cellulose-mercerisation.* Combination of the fibrous cellulose with the alkaline hydrates is associated with profound structural modifications, which are controlled in industrial application to take effect in the increased lustre and fulness of mercerised fabrics.

All the above are synthetical derivatives. In the first group, there is a very large increase of weight. In the other groups there is integral combination and the cellulose recovered by decomposition or otherwise maintains its weight and colloidal characteristics.

Contrariwise, as a carbon compound cellulose is combustible and burns (combining with oxygen) to ultimate products, carbonic acid and water. As a "carbohydrate" (with its hydrogen/oxygen ratio 2/1), it is a highly elaborated complex of unit groups, of C_6 dimensions, which are also carbohydrates; consequently its reactions of decomposition are infinite. Many of the latter are of importance in the study of the actual constitution of the cellulose components, especially those which determine proximate resolution to biose and monose sugars.

Beyond these are further resolutions to compounds of C_1, C_2, C_3, C_4 dimensions, of which perhaps the most important is the bacterial resolution to acetic acid, butyric acid, and alcohol, accompanied by gaseous bodies, H, CO, CO_2, CH_4.

As there are two aspects of our subject matter connoted by the terms "cellulose" (the comprehensive conception) and cellulose (the precise conception of a substance of specific composition and properties, chemical and physical), so we can briefly tell the story of each.

Up to the middle of the nineteenth century "cellulose" was developed in our country through the technology of manufacture and applications. Thus to "spin" the cotton hair, *i.e.* a complex of the hairs, of minute dimensions to a thread or yarn of 200 miles to the 1-lb. represents a very long history of investigation, of applied science, and invention; and the seat of this industry, Lancashire, with Manchester (Cottonopolis) as centre, has been the cradle of generations of craftsmen, as of individuals conspicuous as pioneers of the industry.

The linen and damask industry of Belfast and district also achieved its position of distinction in the industrial world through craftsmanship of a high order, based upon applied science. The jute industry of Dundee is another illustration of technical industrial enterprise, and of appropriation of exotic raw material in building up a flourishing commercial development.

The paper-making industry has steadily expanded, *pari-passu* with national growth, and represents a progressive development of craftsmanship and of applied science.

Up to the middle of the nineteenth century this industry subsisted, *qua* raw material, upon cellulose wastes and rejecta. With increasing consumption and progressive exhaustion of the supplies of raw material arose the necessity of discovering new sources, with the indication that other vegetable fibrous matter must be treated by chemical methods for isolating and purifying the cellulose, to supply "pulp" or half-stuff in massive quantity. A notable contribution was the discovery of esparto, the methods of economic treatment, and the exceptional paper-making qualities of the fibre (cellulose), which we owe to the pioneer labours of Thomas Routledge (1860–1870).

The treatment of the raw material by digestion with alkaline lye (NaOH) resolves the complex structures of the grass; the washed fibrous residue (40–45 %) is bleached to cellulose (half-stuff), the waste lye containing the non-cellulose is concentrated by multiple effect evaporation, and transferred to an incinerator, and the combustion of the organic matter supplies the heat energy for driving off the residual water. Sodium carbonate is extracted from the residue and causticised for re-use.

From the records of importation, the consumption of esparto grew in its first decade, 1860–1870, to 100,000 tons, and in the second, 1870–1880, to 200,000 tons, at which figure it has remained with curious uniformity. It is also noteworthy that "esparto papers" have not been produced in any quantity in other countries.

Following this came the more important development of cellulose supply through the chemical treatment of the coniferous woods. The natural raw material in this case is massive. It is resolved by both alkaline and acid processes of digestion; of the latter, one only—sulphurous acid—by reason of a specific reaction of synthesis (sulphonation)—effects a complete separation of cellulose from the soluble sulphonated non-cellulose. The acid is used in combination as bisulphite (lime, magnesia). This process has been developed on world-wide lines, and mainly in the wood-producing countries, but this country has also played its pioneer part in the industry. The firm of Thomson Bonar and Co., with George Fry, interested in the Scandinavian timber trade, investigated the chemistry of hydrolytic treatments of wood, in association with C. D. Ekman; from this enterprise was evolved the Ekman process (magnesium bisulphite) (1882–1884). The wood-cellulose (pulp) produced in Sweden was not established as a staple paper-making raw material (half-stuff) without the further enterprise of this group in practically demonstrating its qualities, for which a paper mill was equipped at Ilford.

In the competitive extension of the industry which rapidly followed, Edward Partington (of Glossop) took a prominent part, perfecting the chemical engineering of the process and also devoting his great capabilities to the not unimportant commercial pioneering of the industry. The Kellner-Partington Co. is a monument of his success.

The growth of the importation of wood pulp (United Kingdom) in the period 1887–1924 is a steady increase from 80,000 to 1,000,000 tons, and the world's production is estimated at this date at 5,000,000–6,000,000 tons.

In the period under consideration, 1880–1890, there were other tributaries to the general stream of progress in the scientific-technical development of cellulose. Cross and Bevan were publishing researches in the *Journal of the Chemical Society* and the *Journal of the Society of Chemical Industry* (ligno-cellulose–oxycellulose), and assisting the Ekman Fry group in investigating the bisulphite process, and Lawes and Gilbert in studying the cellulose com-

ponents of grasses. The *Kew Bulletin* has many records of investigations of fibres, in which the Economic Botanists of Kew were assisted by the firm of Ide and Christie and the histological studies of John Christie of that firm.

The Colonial and Indian Exhibition (1886) afforded an opportunity of applying new methods to the systematic examination of its collection of vegetable fibrous raw materials. Such new methods based on the classic monographs of Hugo Müller ("Pflanzenfaser. Wiener Ausst. Ber.") and Vetillart (" Études Fibres Textiles "), and developed by the researches of Cross and Bevan, are embodied in the author's report, " Miscellaneous Fibres " (*Reports*, Col. Ind. Ex., London, 1887), and were adopted in the laboratories of the Imperial Institute, which, under Wyndham Dunstan, has continued the research work in this field to the present time. This brief retrospect of the fifty years of the modern development of the subject is concluded by reference to the foundation of special Research Institutions in connection with the textile industries of cotton (Shirley Institute), flax, jute, and the paper-making industry (Paper-makers' Association—Technical Section).

The publications of these bodies are evidence of research work of a high order, scientific in the recognised sense of the term. Empiricism has done its useful work in this field. Future progress will not merely be of industrial developments, but reciprocally these will contribute to the growth of science.

According to our definition, the development of Cellulose, in the second aspect, has been that of physico-chemical investigation and through derivative compounds.

In order of time and of importance in the affairs of the world, we first note in our briefest terms the evolution of the nitric esters—" nitrocelluloses "—from their discovery by Schönbein (1846), through the period of displacement of gunpowder (1) as disruptive or blasting explosive, and (2) as controlled or restrained explosive fulfilling all the conditions for employment as a propellant.

The contrast of explosive effect of the (fibrous) nitrocellulose and the mixture known as gunpowder is expressed in scientific terms as follows :

	Gunpowder.	*Guncotton.*
Solid residue	56·6% (Smoke)	— (Smokeless)
Calories/kilo.	574	898
Temperature	2537° C.	2391° C.
Gas vol., litres/kilo. (calc. at 0° and 760 mm.)	286	887
Gas pressure, kilo./cm.^{2}	409	1145
Explosion velocity m./sec. (in mass)	300	6383
Kinetic effect, kilo./m./sec.	4587	2,076,589
Gas products : composition — CO_2	22·8	30·8
CO	10·0	36·5
N	10·3	16·1
H		1·2
H_2O		15·4
		100·0

In establishing the exact science of the subject, British chemists took a prominent part—W. Crum and Hadow in its special chemistry; Frederic Abel, in the further investigations required in relation to manufacture and applications of the product. His methods of pulping the fibrous nitrocelluloses by wet beating and compression to blocks and slabs were directed towards the control of explosion necessary for use as a propellant; incidentally towards the purification of the product and rendering it stable (Abel's elaborate researches were published in 1866–1867).

A definitive stabilisation treatment was not adopted till 1873, and it rested on a basis of empiricism until 1901, when it was shown that the primary cause of instability was the presence of sulphuric ester (SO_4H) residues in combination (Cross, Bevan, and Jenks, 1901; Hake and Lewis, 1905). R. Robertson further improved the stabilisation processes by a specially designed treatment for the elimination of these residues (Waltham Abbey, 1905).

Reverting to the main development of these products as military explosives, Abel had given indications of the effect of solvents in gelatinising the fibrous nitrocellulose. W. F. Reid produced a partly gelatinised grain powder for shot-guns in 1882. It was not, however, till 1888 that F. Abel and J. Dewar " published " the perfected " cordite " ammunition.

In cordite and in ballistite (Alfred Nobel, 1888) the nitrocellulose is associated with " nitroglycerin," also a " high explosive," but a (liquid) solvent of the former. When milled together the mixture becomes a structureless plastic colloidal mass, which can be moulded at will into the various forms which complete the control of the material as a propellant.

Later developments belong rather to the specialist technology of explosives, and the colossal proportions of the industrial production of this material for the Great War 1914–1918 is evidence of the dominating position of cellulose for destruction as well as for constructive evolution.

In this period, the researches of R. Robertson and his associates led to the production of perfected types of cordite through methodical scientific diagnosis of the properties of cellulose in relation to the qualities (stability, etc.) of the primary constituent, the nitrocellulose.

The other applications of the nitrocelluloses, viz. to the manufacture of celluloid (films and massive solids) and the first of the artificial silks, can only be mentioned, since we cannot claim for Britain any pioneer part in their development.

Next in order of importance is the invention of viscose (1892) and the development of its industrial applications from 1895 to the present time in progressively increasing dimensions. For the full scientific-technical history of the discovery in its applications readers are referred to the *Journal of the Textile Institute*, Mather Lecture, 1922, C. F. Cross.

The viscose reaction is a synthesis in two stages, viz. (1) alkali cellulose—cellulose and NaOH, (2) alkali cellulose and CS_2, to cellulose xanthogenic acid (alkaline Na salt). The normal cellulose is integrally converted to this form, soluble in water to viscose and quantitatively recovered by spontaneous decomposition (in mass—to be finished as solid " viscoid "), or by reactions which condition regeneration in the form of film (cellophane) or thread, the latter constituting the most important of the artificial silks.

In association with the above and with various and obvious connecting links, we mention the alkali-cellulose reaction of John Mercer (1850), which, though very fully investigated by this pioneer worker, was accorded an incubation or sleeping period of thirty to forty years. Reinvestigated in regard to textile effects by H. Lowe in this country, it was rapidly developed to the industrial production of " mercerised " cotton fabrics with their characteristics of silky lustre and finish. Studied by Cross and Bevan in relation to the reaction effects and modifica-

tion of the cellulose complex, the result was the viscose reaction, followed in duly deferred sequence by its industrial applications.

In order of recognised importance, but long antedating " viscose," is the solution of cellulose in " cuprammonium " (solution of copper hydroxides in aqueous ammonia). The discovery of this reaction is attributed to E. Schweizer (1857), but the earliest systematic investigations are those of Mercer. The reaction effects were applied by Scoffern (1869) to waterproofing paper and textiles. In this country, there followed (1880) a more systematic industrial development of these effects by a limited liability company with a factory located at Willesden, Middlesex, which successfully produced " Willesden " goods over a long period. The undertaking owed its methodical and economic production of the solvent to C. R. Alder Wright, and its technical commercial success to A. Healey. These processes are based upon the effects of colloidal hydration and partial solution. Later in the century, and with the purpose of producing an artificial (cellulose) silk, to compete with the first of these products (from nitrocellulose, H. de Chardonnet), the conditions of reaction were perfected to the point and result of furnishing a solution of cellulose fulfilling the requirements of the new industry. The production of artificial silk and filaments (Glanzstoff) by this process was rapidly developed in Germany.

We have thus briefly noted the origin and early stages of the three established industries in artificial silk, in which the product is a modified cellulose in the form of a structureless colloid. These industries have largely extended our knowledge of the parent substance, and in fact developed the potentialities of cellulose represented by its unique properties as an individual, and its place and function in the natural order.

The *cellulose acetates* are legion. Not only are the stages of acetylation of the order of a progressive series, but the associated changes of the cellulose complex are variable with all the conditions of reaction.

At the ascertained maximum of esterification, $C_6H_{10}O_5$ becoming $C_6H_7O_2 \cdot 3OAc$, the ester is soluble in chloroform and certain other solvents, but of limited range. Prepared by special processes, it retains the structural characteristics of the parent substance.

The production of such acetates on a manufacturing scale was first achieved by Cross and Bevan and developed by C. O. Weber in this country (1894–1899); but the first realisation of industrial results is that of the British Cellulose (now " Celanese ") Co. working the patents and processes of H. and C. Dreyfus.

These processes are specially directed to the production of acetone-soluble ester. This is the basis of an important application to textiles giving a shrunk waterproof finish which has been applied on a very large scale to the treatment of aeroplane parts. The production of silk and thread has the exceptional feature of applying the ester, *as such*, to these uses.

An additional feature is that the ester-substance is of lower specific gravity than any form of cellulose. The product has established an industrial position, but the developments are limited.

A brief mention of the last of the products noted on p. 161 is required to emphasise a special feature of the solution of cellulose by zinc chloride. It is evident that in this case there can be no contribution of effect from a disturbance of oxygen equilibrium; nor can there be any specific reaction with the carbonyl groups of the cellulose units. The complete dissolution of cellulose in the aqueous solution is a particular case of the general reaction of cellulose as an amphoteric colloid reciprocally with the components of inorganic salts.

In all the developments above noted and described we are dealing with cellulose as such, and in the derivative or artificial forms the fundamental properties of the complex are maintained, so that these bodies are to be regarded as actual cellulose derivatives. There are indications, however, that in certain of the treatments for the production of synthetical derivatives the cellulose complex is affected, and the derivative has indications of lower-grade properties. This is seen in certain of the acetic ester products, and it is also seen in a series of derivatives, ethers, in which the OH groups are progressively replaced by methoxyl and ethoxyl. In a large number of industrial processes this tendency to break up is in evidence (" oxycellulose "-" hydrocellulose "). The literature of these reactions is too vast for mention.

We conclude by a brief notice of processes which resolve the cellulose to ultimate groups of the carbohydrate series, or beyond this to compounds of C_5 to C_1 dimensions.

The controlled resolution of cellulose to sugars of definite constitution and configuration has been applied by J. C. Irvine and his co-workers to advance in a very important way our knowledge of the actual molecular structure of the cellulose complex. This is an obviously primary objective of scientific research, and contributions of this school (St. Andrews University) of research, under J. C. Irvine, have taken first rank.

The more destructive resolution of cellulose to gaseous and liquid products plays a very large part in the natural organic world, and in later years the actual mechanism of the processes, especially where they depend upon bacterial agency which can be controlled, has been closely investigated. We can only mention as an important achievement in this country the control of such bacterial processes to requirements of the industrial production of the main products, such as acetic acid, alcohol, etc. This is due to a corporation, Power Spirits, Ltd., and the scientific technical investigations of H. Langwell of that corporation.

This matter has now reached the stage of operation on a large scale, and appears destined to play an important part, not only in industry, but also in contributing to the development of the pure science of this vast subject.

COLOUR IN NATURE

By Reginald Furness, M.Sc.

The natural colouring matters possess for the chemist an interest which is more than commensurate with their commercial importance, and experimental work continues to be effected in the determination of structure and in the subsequent synthesis of nature's colouring principles. The isolation, characterisation, and synthesis of the colouring principles of flowers does not complete the enquiry, however, for the life-processes of the plant demand study, and the relations which have been traced between colour formation and enzymic activity, for instance, demonstrate the real complexity of the apparently simple process by means of which the flower builds up beautiful colour effects.

Plant Colouring Matters.—It would prove wearisome to catalogue the hundreds of dyestuffs which man has employed, with the help of mordants, to dye his textiles, etc., from the most ancient of times up to the time of Perkin's discovery of mauve, when a new era in dyestuff chemistry commenced. A few important examples may be given in natural indigo, madder, logwood and other woods, turmeric, fustic, quercitron bark, and Persian berries. With the rise and development of the study of organic chemistry in the first half of the nineteenth century, much attention was directed to the extraction and characterisation of pure colouring matters from natural sources—usually the bark, leaves, fruits or sap of trees or plants. During the twentieth century—and just a little before—great progress has been made in the synthesis of many typical natural colouring matters, and the improved technique and novel synthetical methods will bear upon the general progress of chemistry.

Chlorophyll.—Chlorophyll is the green colouring matter which exists in the leaves and other parts of plants, usually in association with the yellow carotin and the brownish-red xanthophyll. These plastic pigments occur colloidally in the protoplasmic structure of the plant, and differ from the typical soluble sap pigments, such as the flavones and the anthocyans, which are discussed later.

Chlorophyll possesses useful as well as decorative functions in the plant, for it is intimately concerned in the assimilation of carbon dioxide, and the interaction of the latter with water and nitrogen compounds, by means of which the cell structure of the plant is built up. In this connection, the study of the photocatalytic activity of chlorophyll—as well as of carotin and xanthophyll—at the hands of Baly, Heilbron, and the Liverpool school must be mentioned.

The extraction of impure chlorophyll, suitable for technical use in the colouring of fats, oils, soaps, salves, perfumes, and various alcoholic preparations, etc., is simple. The plant is exhausted with ether, the solution evaporated, and the residue treated with alcohol, in which the chlorophyll is readily soluble. The pure chlorophyll required in the researches of Willstätter, described later, is only obtained by much more careful elimination of the wax, starch, etc., present in the original extract from the plant.

The investigations into the complex problem of the constitution of chlorophyll have possessed an attraction for chemists for many decades, and the pioneer work of Schunck and the Manchester school, and of others, should not be forgotten when we come to examine the brilliant researches of Willstätter and his co-workers. The formation of the blue phyllocyanin and of the yellow phylloxanthin of Fremy and Schunck, and the general indications that the far-reaching decomposition of chlorophyll led to pyrrole derivatives, are typical results of investigations which gave an insight into the composition of chlorophyll long before the actual pigment had been isolated in a pure condition.

The exhaustive treatment of the subject by Willstätter has made it possible to advance a structural basis for the molecule of chlorophyll, which, even if it become modified in future, nevertheless represents a great forward move.

As it would require the whole of the space of this chapter to discuss fully a tentative constitutional formula, let us confine ourselves to the important issues which centre around the presence and location of magnesium in chlorophyll, and the existence of two distinct forms, namely, chlorophyll *a* and chlorophyll *b*.

By a series of decompositions, effected by means of alkali in alcoholic solution, chlorophyll gives the chlorophyll green acids, the chlorophyllins, which have been obtained in a pure condition, and shown to be magnesium compounds, in which the metal is bound to the nitrogen, the linkage being of a complex nature. By further decomposition of the chlorophyllins, through the agency of alcoholic alkali at 240° C., the phyllins are produced and have been isolated as crystalline individuals. These substances still contain magnesium, and are free acids with progressively smaller numbers of carboxyl groups. Finally, the last carboxyl group can be eliminated, and a compound, still containing magnesium, namely ætiophyllin, $C_{31}H_{34}N_4Mg$, obtained. The magnesium is not, therefore, present in a carboxyl group in the chlorophyll molecule, and there are only nitrogen-containing groups available for the binding of the metal.

Willstätter has definitely shown that the magnesium content of the chlorophyll extracted from a very large number of land- and sea-plants is constant.

By gentle decomposition of chlorophyll * by means of oxalic acid, the magnesium section of the molecule is detached and in this way phæophytin can readily be produced in relatively large quantities for examination. This substance is precipitated from an alcoholic extract of green leaves and is obtained free from the colourless and yellow substances present in the leaves. Phæophytin does not contain magnesium, and the splitting off of the metal is the only change which occurs when the preparation of the plant material, the extraction, and the treatment with acid are skilfully effected. Phæophytin is a wax-like substance, without acid properties, and is, in fact, weakly basic in character. The similarity of this decomposition product to chlorophyll is evident as soon as a metal is introduced into its molecule. Although it is somewhat more difficult to introduce magnesium than, say, copper or zinc, into this decomposition product of chlorophyll, it has been successfully accomplished by Willstätter by the use of the Grignard reagent, magnesium methyl iodide. A similar reaction may be effected upon other decomposition products of chlorophyll. Thus, phylloporphyrin, $C_{31}H_{35}N_4{\cdot}COOH$, under the influence of acid and magnesium methyl iodide yields the magnesium containing phyllophyllin, $C_{31}H_{33}N_4Mg{\cdot}COOH$.

The above brief discussion may serve to render comprehensible the following group formula for the colouring matter, namely, $[C_{31}H_{29}N_3Mg](NH{\cdot}CO)(CO_2{\cdot}CH_3)(CO_2{\cdot}C_{20}H_{39})$—chlorophyll *a*. For a full consideration of the assumed atomic linkages, the lactam ring which serves as a chromogenetic grouping in the molecule, the tentative structural arrangement of the molecule, etc., the original papers of Willstätter *et alt.* should be consulted, whilst, as a general review of the whole work, the article by Willstätter (*J. Amer. Chem. Soc.*, 1915, **37**, 323) will be found of great interest.

* The question of the two forms of chlorophyll, *a* and *b*, and therefore of the two series of decomposition products, differing only slightly in composition, will not be discussed at this stage, and chlorophyll will be regarded for the sake of simplicity as a single substance.

Passing to a consideration of the proof that two forms of chlorophyll exist, namely, chlorophyll *a* and chlorophyll *b*, Willstätter showed that, in carefully controlled decompositions of phæophytin, two, and only two, crystalline and characteristic substances, namely, phytochlorin *e*, $C_{34}H_{34}O_5N_4$, and phytorhodin *g*, $C_{34}H_{32}O_6N_4$, are produced. These substances are not fragments produced by the breaking up of the phæophytin molecule, for their molecules are of the same order of magnitude as that of phæophytin itself. They are not inter-convertible, and are formed in definite weight proportions. One of them cannot represent, therefore, an earlier, and the other a later, stage of the decomposition of phæophytin. Thus, the formation of two distinct decomposition products of this nature demands the assumption that phæophytin and consequently chlorophyll itself, is a mixture of two components, one of which furnishes phytochlorin *e*, and the other phytorhodin *g*.

The two components of chlorophyll can be separated by dividing them in an unequal manner between two solvents, say, methyl alcohol or aqueous methyl alcohol and petroleum ether. By systematic fractionation and continued rearrangement of the relative proportions of the components in the immiscible solvents, a final separation of perfectly homogeneous chlorophyll *a* and chlorophyll *b* results.

Chlorophyll *a* is bluish-green in appearance, and chlorophyll *b* is yellowish-green, and in spite of differences in optical behaviour, their compositions are only slightly different. The latter and its derivatives may be assumed to be derived from the corresponding *a* compounds by the replacement of two hydrogen atoms by one oxygen atom,* and the formulæ suggested are respectively $C_{55}H_{72}O_5N_4Mg$ (*a*) and $C_{55}H_{70}O_6N_4Mg$ (*b*).

Willstätter and his associates have so developed their experimental procedure that they can isolate a pure chlorophyll product in a few hours from dried leaves, with a yield of about 80 % of the theoretical, or, say, about 6·5 grams from 1 kilogram of dried leaves. Thus, they have been able to demonstrate the identity of the chlorophylls existing in a large number of different land- and sea-plants, in which the relative proportion of the *a* and *b* varieties of the colouring matter may differ considerably. In addition, the relative amounts of chlorophyll and the associated carotinoid pigments present in green leaves and in marine algæ, respectively, are not the same.

Natural Indigo.—The first use of natural indigo as a dyestuff takes us back to remote antiquity, but it was not until the seventeenth century that its use became widespread in Europe. It is interesting to note that about this time English dye-makers, producing woad from home-grown plants, were as much exercised as are their fellows to-day, manufacturing synthetic dyestuffs, regarding the importation of the foreign dyestuff indigo. In fact, indigo was banned the country for a considerable period in response to the agitations of the woad producers.

Natural indigo to-day is gradually being ousted by the synthetic substitute, indigotin, but a brief outline of the process of manufacture may be given, for it is still carried on to no inconsiderable extent.

Indigotin exists in the plant *Indigofera tinctoria* and other plants, in the form of a glucoside, indican. The plants are first steeped in water for some time, when fermentation occurs and the liquor is now drawn to oxidation vats, where it is agitated by means of paddles, mechanical stirrers, or compressed air. Indigo is precipitated following the oxidation which occurs.

* Compare, for instance, the formulæ for phytochlorin *e* and phytorhodin *g* given above.

Heating is now effected to check further fermentation, and the separated indigo is filtered to give indigo paste. The latter is pressed into cakes and dried.

The fermentation and oxidation processes are not quite so simple as indicated, for other changes take place. Broadly, however, the indican is fermented to give soluble indoxyl, which is oxidised—not quite quantitatively—into indigotin. In commercial indigo there exist, in addition, indirubin, indigo brown, indigo gluten, and mineral matter.

It is merely necessary to refer in closing this brief account to the brilliant analytic and synthetic experiments of Baeyer, to whom we owe the realisation of synthetic indigo. In spite of the great improvements in technique, synthetic indigo may still have to face the competition of natural indigo. If only attention be directed to the controlled bacterial fermentation of the glucoside indican, the quality of the water used, the deleterious acidity of the steeping vats which is possibly capable of being countered by ammonia-producing organisms, the mechanism and control of the oxidation of indoxyl, the selection of soil and locality for the cultivation of the plant, artificial fertilisation, transport, and other problems of commercial and technical importance, it is possible to foresee a reduction in the cost of production of natural indigo sufficiently great to bring the latter into full economic competition with synthetic indigotin. British workers have commenced the task in India, and the recent work of Davis on the nature of the changes occurring during the extraction of indigo, and on the various factors influencing the yield and purity of the indigo obtained, has already shown the possibility of obtaining much higher yields of indigo of superior quality. If only intensive research on these lines be fostered, the threatened extinction of the natural indigo industry may be delayed indefinitely.

Madder.—One of the oldest and most valued of natural dyestuffs was that extracted from the madder root. It was used in ancient India, Egypt, and Persia, and throughout the ages the varied shades which could be obtained with different mordants made madder a prized colouring matter. With the synthesis of alizarin by Graebe and Liebermann in 1868, and the commercial manufacture from anthracene following very shortly afterwards, the cultivation of the madder root ceased almost entirely and at once. To-day, natural madder is unknown in commerce.

Madder contains chiefly alizarin and purpurin, and the latter was extracted (in one method) by means of water, converted into the lime lake and recovered from the latter by acidification with hydrochloric acid. The alizarin was extracted by means of wood spirit, and recovered from the solution by precipitation with water. Other methods were, of course, practised, but require no description at this juncture on account of the disappearance of natural madder colours from commerce.

The characterisation of alizarin and purpurin as dihydroxy- and trihydroxy-derivatives of anthraquinone respectively, naturally came before the synthesis and commercial production of the artificial colours, and represents the only chemistry of madder colours which need be referred to here.

The Flavones.—A wide variety of yellow colouring matters scattered throughout nature has been shown to possess flavone as a basis, and has inspired some of the most interesting and important analytic and synthetic experiments at the hands of English and foreign workers during the last two or three decades. These dyes are hydroxyl derivatives of flavone, and the intensity of the shade, obtained, say, with an aluminium mordant, depends upon the number and position of the hydroxyl groups in the flavone molecule.

Flavone.—Flavone itself has been shown to be present in the yellow dust occurring upon

the flower stalks, leaves, and seed capsules of several varieties of primulas. Thus, Müller in 1915 extracted a substance, $C_{15}H_{10}O_2$, which proved to be flavone from *Primula pulverulenta* and from *Primula japonica.*

Chrysin.—Chrysin is a dihydroxyflavone, found in the leaf buds of the poplar to the extent of about 0·25 %. It dyes wool, mordanted with aluminium, chromium, or iron compounds respectively, in shades of yellow, orange, and chocolate-brown.

Apigenin.—In the form of its glucoside, apiin, this flavone derivative occurs in the leaves, stems and seeds of parsley. It was shown by A. G. Perkin to be a 1 : 3 : 4-trihydroxyflavone, and this structure has been confirmed by Kostanecki's synthesis. Apigenin dyes mordanted wool much in the same shades as does chrysin.

Luteolin.—The colouring matter of weld, *Reseda luteola* (which was one of the earliest natural dyestuffs employed in Europe), is still used for the dyeing of certain army cloths, etc., and for dyeing silk to some extent. Luteolin is a 1 : 3 : 4′ : 5′-tetrahydroxyflavone. With aluminium and tin mordants, it gives bright shades which are reasonably permanent, and it is a much stronger dyestuff than the di- and tri-hydroxyflavone derivatives. Weld is, however, not so strong a colour as quercitron bark or fustic (*q.v.*), and its use is by no means so common to-day as in days past.

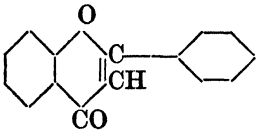
Butin and Butein.—The tree *Butea frondrosa,* growing plentifully in India and elsewhere, produces orange-yellow flowers closely resembling our English gorse. The flowers contain a yellow dye—closely related to the class under discussion—which is used for the dyeing of native garments for religious festivals.

Butein is the dyestuff contained in the butea flowers and is a tetrahydroxybenzylidene-acetophenone, or tetrahydroxychalkone. Butin is the corresponding flavanone compound and is likewise found in the butea flowers.

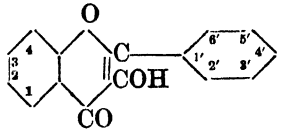
Both butein and butin dye mordanted wool identical shades, but the latter is not really a dyestuff, but a dye principle, converted during the process of dyeing into the true dyestuff butein.

The Flavonols.—Amongst the most widely distributed of natural colouring matters, the flavonols are also the most important natural yellow dyestuffs remaining in use. Such dyes as quercitron bark, old fustic, Persian berries, and others contain flavonols as their essential principles. The class is interesting in addition as being the field of many brilliant synthetical operations.

The flavonols differ from the flavones only in the possession of a hydroxyl group in place of the hydrogen in the γ-pyrone ring. Thus,



Flavone.



Flavonol.

The influence of the hydroxyl group in the pyrone ring is evident upon comparing luteolin and quercetin, both 1 : 3 : 4′ : 5′-tetrahydroxy-derivatives, the former of flavone and the latter of flavonol, with its hydroxyl group in the pyrone ring. Luteolin gives only bright yellow shades, whilst quercitrin leads to the formation of brown-orange shades upon aluminium mordanted wool—the presence of this hydroxyl group thus deepening the colour.

In some cases the flavonol is associated in nature with a sugar, or, in other words, the dye exists in the plant in the form of a glucoside. Thus, quercitrin is the glucoside of the dye quercetin, both the glucoside and the flavonol itself possessing tinctorial properties. Morin exists in old fustic, on the other hand, quite free, and the tinctorial properties of old fustic are due directly to the flavonol derivative. The position of the sugar residue in the molecule may affect the dyeing value of a flavonol glucoside to some degree.

Quercitron Bark.—The yellow inner bark of certain varieties of oak is still used to a considerable extent as a dyestuff. With chromium mordanted wool, the quercitron bark dyes give reddish-brown shades, with aluminium mordants brown-orange shades, with tin mordants bright orange shades, and with iron mordants olive-black shades.

Quercetin and quercitrin come into commerce in various forms, such as the red and yellow flavins, patent bark, bark extract and so forth, and the free flavonol and the glucoside are often found associated in one and the same commercial preparation, according to the method adopted in manufacture. Quercitrin, the glucoside, gives in general yellower shades than does quercetin and both compounds are more popularly employed upon mordanted wool or silk, since the shade upon cotton is somewhat fugitive to light.

Quercetin is also present in onion skins and in heather, but the use of these substances as natural dyestuffs has almost entirely disappeared.

The extract of Persian berries is, however, prepared in considerable quantities to-day. It is employed in calico printing. The ferment present in the berries causes hydrolysis of the quercetin glucoside, so that the extract dyes by virtue of its free quercetin, and therefore gives redder shades than does quercitron bark. The latter, containing no hydrolytic enzyme, dyes by reason of the presence of the glucoside itself, which, as we have seen, gives rise to shades which are not so reddish as are those produced by quercetin.

Old Fustic.—This dyestuff from the wood of the tree *Chlorophora tinctoria* is perhaps the most important yellow natural colouring matter, and is still employed in considerable quantities. It is comparatively little used for silk or cotton dyeing, but with copper, tin, chromium, or aluminium mordants, it is a valuable wool dye. It gives an old gold shade with chromium, an olive-green shade with copper or iron, and a yellow shade with aluminium mordants. Some of the lakes are extremely fast to light, but the yellows are sometimes only moderately so.

The essential colouring principle of old fustic is morin, 1 : 3 : 4′ : 6′-tetrahydroxyflavonol.

The Colour of Flowers and Fruits.—It is manifestly impossible to describe the pigments which are responsible for all the varied colour effects in plants, flowers, fruits, leaves, etc., but there is an important class of soluble or sap pigments, namely, the anthocyans, which presents a great interest. The anthocyan pigments create some of the most beautiful colour effects in flowers, and have been the object of a profound, painstaking, and eminently successful series of researches by Willstätter and his associates.

The anthocyans have attracted the attention and curiosity of chemists and botanists since the days of Berzelius, and although much interesting work has been reported, the greatest step forward came in the isolation of numerous crystalline individuals by the improved methods of Willstätter, and the characterisation of the class of anthocyan pigments.

The anthocyans are all related to three substances, namely, cyanidin, pelargonidin, and delphinidin. The red, blue, and violet colours of flowers are due to the presence of these substances, their methyl derivatives, or their glucosides. The latter are known as the cyanins, pelargonins, and delphinins respectively, and are by far the most common form of the anthocyan

pigments, it being comparatively rare that the free anthocyanidins occur in flowers. Even in these instances, the amounts are relatively small as compared with the amounts of the glucosides.

The glucosides are formed from the anthocyanidins and either dextrose, rhamnose, or galactose. Dextrose is the principal sugar found, whilst galactose only occurs in a single instance. The wide variety of the anthocyans is dependent upon variations in the nature and number of the sugar residues and to differences in their position in the complex molecule—in their points of attachment to the anthocyanidin nuclei.

The colour of a particular flower depends, not only upon the particular anthocyan or anthocyans present, but also upon the concentration, the nature of the cell sap, the presence of other bodies such as tannin, iron salts,* organic acid, enzymes, etc. In addition, the anthocyans may exist in the plant either in the free state, as salts, or as oxonium compounds with mineral or organic acids. In these respective conditions, the anthocyans form the basis for violet, blue, and red shades.

As an instance of the variation in the amounts of pigment present in flowers, the following figures are of interest. Cyanin, the colouring matter of the blue cornflower, exists in the dried petals to the extent of 0·7 %. The same pigment occurs in the dark red garden variety to the extent of 14 %. Again, violanin, the glucoside of delphinidin with rhamnose and dextrose, forms the colouring matter of the violet pansy, the dried petals of which contain 33 % of their weight of the anthocyan.

A list of some typical anthocyans is given here, and the extent of their occurrence in nature will become apparent if it be remembered that, in addition, scores of other glucosides have been prepared in a pure state, following extraction by water or dilute alcohol, fractional precipitation, crystallisation, and so forth. It will also be apparent that the same anthocyan may occur in flowers and fruits of widely different colour.

Cyanin.—Cyanin occurs in the blue and dark red cornflowers, the rose, dahlia, and in some pelargonia. It is found in the bilberry and black wild plum, and an isomer, mecocyanin, is largely responsible for the colour of the scarlet poppy. Both cyanin and mecocyanin are derived from cyanidin, dextrose being the sugar present in the glucoside.

Asterin and Chrysanthemin, found in the aster and chrysanthemum respectively, are isomeric glucosides from cyanidin also, but contain only one dextrose residue in the molecule of the pigment, whereas cyanin contains two.

Keracyanin and Prunicyanin again are isomeric with the cyanin of the cornflower and the mecocyanin of the scarlet poppy respectively, but differ in that they contain two rhamnose residues. These glucosides are present in the cherry and sloe respectively.

Delphinidin glucosides occur in the larkspur, wild mallow, and pansy, whilst the corresponding glucoside of delphinidin dimethyl ether, namely, *œnin*, is found in wine. The glucoside is present in the skin of the grape in conjunction with the free delphinidin, namely, œnidin—a circumstance which is by no means common.

Violanin.—This anthocyan presents us with an instance of two different sugar residues in the molecule, dextrose and rhamnose. The parent anthocyanidin is delphinidin.

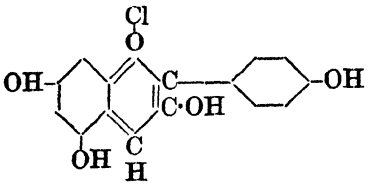
The anthocyan pigments have been employed in the past for dyeing purposes, but the colours obtained upon textiles were mostly fugitive. To-day, for reasons which are obvious, they have no commercial significance.

* Compare the blue and pink varieties of *Hydrangea hertensis*, grown by Atkins in soils of p_H 5·7–6 and above 7·5 respectively. The blue flowers contain 140 parts and the pink 60 parts of iron per million.

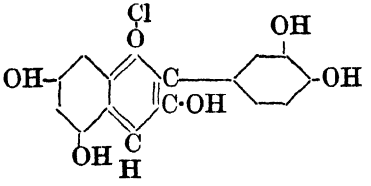
It is impracticable to enter here into a full discussion of the constitution of the anthocyanins and their parent anthocyanidins, but it may briefly be stated that they resemble the important flavonols, the yellow colouring matters discussed above. They may be regarded as reduction products of the corresponding members of the flavonol series.

From the point of view of colour, it is of interest that, as in the case of the flavonols, the anthocyans become darker as the hydroxyl content of the molecule increases, from pelargonin through cyanin to delphinin.

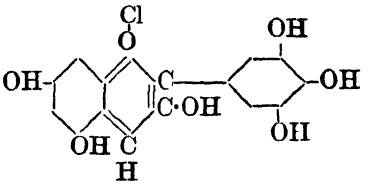
These points will become clearer when the following formulæ for the three basic anthocyanidins are considered :



Pelargonidin Chloride.

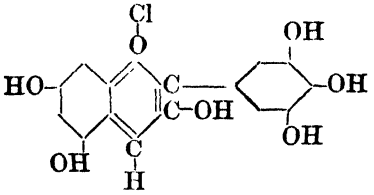


Cyanidin Chloride.

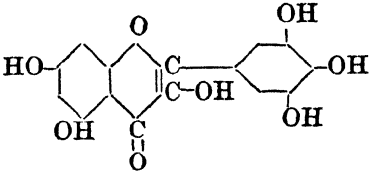


Delphinidin Chloride.

The intimate relationship between the anthocyans and the flavonols will be noticed by an inspection of the following formulæ, which represent typical anthocyans and flavonols respectively. The formulæ first suggested by Everest have been confirmed by synthetical experiments at the hands of Willstätter and others.

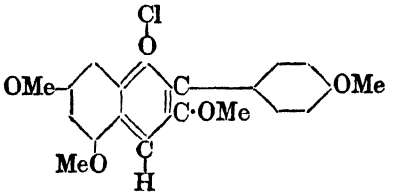


Delphinidin Chloride.

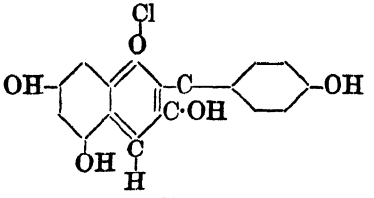


Flavonol Derivative.

Robinson's recent work in this field has brought forward novel methods of synthesis, which are typical of the beautiful work of this brilliant investigator. Pelargonidin chloride was synthesised from 2-hydroxy-4 : 6-dimethoxybenzaldehyde and 4 : ω : dimethoxyacetophenone, which reacted in ether in the presence of hydrochloric acid to give tetramethoxypelargonidin chloride (1). By subsequent demethylation, pelargonidin chloride (2) was readily obtained.



(1)



(2)

The Formation of Pigments in Flowers.—The apparent simplicity with which plants synthesise the pigments responsible for the infinite variety and gradations of colour effects

stands in strong contrast to the laboured efforts of the chemist to manufacture artificial colouring matters. The processes by which pigments are produced, in common with the general life-processes of plants, are, however, complex, and do not always receive from chemists the attention and study they merit. It is fitting, therefore, to indicate briefly the function which enzymes perform in the formation of flower pigments, since, although there are other important questions pertaining to this study, the *rôle* of oxydases has been determined with care and precision.

Pick, in 1883, first suggested the hypothesis that oxydases are concerned in the formation of pigments in plants, and several observers have supported this theory. In 1910, Miss Wheldale suggested that the colourless chromogen, by the oxidation of which a pigment is produced, occurs in the plant in the form of a glucoside. Enzymes of the emulsin type hydrolyse the glucoside, itself resistant to oxidation, and the free chromogen is then oxidised by atmospheric oxygen, activated by an oxydase.

The definite proof of the intimate connection between the presence of oxydases and the formation of pigments in the various parts of the plant has been afforded by the work of F. Keeble and E. F. Armstrong. The isolation of glucosides as the principal constituents of the anthocyan pigments may demand a modification of the hypothesis of Miss Wheldale (or, alternatively, it is conceivable that the pigment produced according to this view of the process may subsequently combine with a sugar through the synthetic influences of enzymes), but, in any case, the explanation of the function of oxydases is secure upon the basis of the work of Keeble and Armstrong.

These investigators first established a trustworthy test for the presence of oxydases (and peroxydases). Alcoholic solutions of benzidine and α-naphthol were found to give specific colour reactions with oxydases, the petal or other part of the plant being first decolorised by the reagent and then stained a rich dark brown when benzidine is used, α-naphthol producing a lilac blue or lavender. The addition of hydrogen peroxide may be required, and in some instances with benzidine, a temporary blue or blue-green colour may form prior to the development of the characteristic brown formed in the cell structure. Benzidine, moreover, registers the presence of oxydases in the epidermis of the petal, whilst both benzidine and α-naphthol react with oxydases present in the cells constituting the bundle sheaths. It is emphasised, too, that negative results must be accepted with caution, for, as will appear later, certain flowers contain inhibiting substances, which prevent the formation of the characteristic test colours.

With the aid of this valuable test, it has been clearly demonstrated that, in general, the distribution of pigments in flowers coincides exactly with that of oxydases. The oxydases, it is true, are more widely distributed than are the chromogens, but the distribution is in conformity with the oxydase–chromogen hypothesis, as will be illustrated by several typical examples, culled from the many available.

The flowers of *Primula sinensis* and of *Dianthus barbatus* (Sweet William) show most epidermal oxydase in the most deeply coloured varieties, less in the less deeply coloured, and none at all in the white varieties. The white flowers of certain *P. sinensis*, *Pisum sativum* and *Lathyrus odoratus* have all been shown to contain oxydases, and the white colour is attributed to the absence of chromogen. In the Mont Blanc Star, the distribution of oxydase again parallels that of pigment. One flower had irregular magenta flaked petals with one exception, this particular petal being of a uniform magenta colour. The latter petal gave a well-marked

oxydase reaction, the magenta patches on the others demonstrated a fair reaction, whilst the white portions did not respond to the test.

Similarly, Sweet Williams were grown in full-coloured, white, and almost white varieties, the latter showing rosy dots or lines. The fully-coloured flowers responded definitely to the tests for the presence of oxydases, whilst the white flowers also gave a definite but limited reaction—the white colour being probably due, as explained above, to the absence of chromogen. The white flowers with rosy dots showed oxydases only in the parts of the petals corresponding to the pigmented dots.

Space forbids a full discussion of the interesting subject of inhibitors, and it must suffice to say that reagents were discovered, such as hydrocyanic acid solution and carbon dioxide solution, which destroyed the influence of these substances, and allowed the oxydases present to respond to the specific tests noted. The investigations upon white primulas, and upon specially cultivated varieties possessing white zones upon a blue ground, and on other white flowers, which are also known by breeding records to be in the class of dominant whites, conclusively support the Mendelian hypothesis that the dominant white flowers contain no pigment by reason of the presence of inhibitors of pigment formation. Inhibition is exercised upon the oxydases and not upon the processes which result in chromogen formation. Again, the inhibitors, as the name implies, do not destroy the oxydases, but merely interfere with their otherwise normal activity.

The recessive white varieties are those, noted above, which owe their lack of pigment to the absence of chromogen and not of oxydase.

Although the questions of localisation of oxydases, effects of light and darkness upon the development of oxydases, and other vitally important matters cannot be discussed here, enough has been written to indicate the accuracy of the views of Keeble and Armstrong on the important *rôle* of oxydases (and peroxydases) in the formation of flower pigments. Much remains to be done before the full mechanism of the life-processes of the plant responsible for colour development is revealed, but an important step forward has been made.

It only remains to be added that substantial confirmation of the views of Keeble and Armstrong has been forthcoming in the work of Atkins. This investigator has shown the presence of oxydases and inhibitors in the petals of the iris, the colours of which are due to the presence of a yellow, plastic pigment and an anthocyan or anthocyans. The general distribution of enzyme and pigment in the iris resembles that in *Primula sinensis*.

Origin of Colour Effects in Nature.—The ultimate reason why any object appears coloured to the eye is bound up, of course, with the phenomena of light absorption, reflection, refraction, etc., but we are accustomed to regard colour as a result of the presence of a pigment. Thus, it is quite true that the colours of many of our most beautiful flowers are directly occasioned, as has been shown, by the presence of the anthocyan pigments, which can be extracted and identified as definite chemical entities. The colouring of many birds' feathers, the blue colour of the sky, the sunrise and sunset tints, and the colour of blue eyes are all directly the result of light phenomena. The actual final effects may be modified by the presence of a dark pigment, which often serves as background, or by the presence of a yellow pigment which, superimposed over a structural blue, results in a structural green colour. For the purpose of broad contrast, however, we may regard the colour of flowers as due to the presence of pigments and that of blue feathers as due entirely to light effects, produced in the absence of pigments. The latter, the so-called structural colours, are divided into objective

structural colours and subjective structural colours, the former being caused by the scattering of blue light by a turbid medium and being independent of the angle of incidence of the light. Subjective structural colours, on the other hand, are due to light interference phenomena, as in the case of the coloured "Newton's rings," and are responsible for the brilliant flashing colours showing a metallic lustre and seen, for instance, in the tail feathers of the peacock.

Blue, Green and Iridescent Colours of Feathers.—The blue and green colour of birds' feathers is due entirely to the scattering of blue light by the disperse system constituting the feathers, with the aid of a yellow pigment superimposed upon the feather structure in the case of green colour effects. Thus, no blue pigment can be extracted from the feathers of the blue bird, the blue jay, the kingfisher, or the indigo bunting. The blue light, incident upon the feathers, is scattered by the disperse system consisting of minute air cells in the horny structure of the feathers, the former representing, of course, the dispersed substance and the latter the disperse medium. The air cells or pores exist in the outer layers of the barbs of the feathers. The blue colour observed is the ordinary "Tyndall blue," and is common in turbid media, such as the sky and the human eye, as well as in many natural minerals and artificial glasses and porcelains, etc. The blue of the sky is, according to Bancroft, due to light scattering in the disperse system, which, contrariwise to that of feathers, consists of a gaseous dispersion *medium* and a solid disperse *phase.*

The theory of the cause of the blue colour of the feathers of the birds noted above fits into the general conception of the scattering of blue light by disperse systems. The latter are of three classes, namely, a solid in a gas (as in the case of the sky), a gas in a solid (as in the case of blue feathers) and a liquid or solid in a liquid (as in the case of blue eyes).

Before passing to a consideration of the iridescent colours of birds' feathers, a short account of the scattering of light by the first and third noted disperse systems may be given.

The Blue of the Sky.—The blue colour of the sky has been attributed to the phenomenon of light scattering since the time of Leonardo da Vinci, but even to-day the *exact* mechanism is under discussion. It has been suggested that the scattering is effected by finely-divided solid particles or dust, suspended in the air, whilst finely-divided water particles may provide an alternative explanation. Artificial blue "skies" have been created in disperse systems of solids in gases. Nicholl states, however, that whilst there are reasons for regarding the sky as a turbid medium—a disperse system—experimental observations on the spectrum of sunlight cannot be entirely explained by the assumption of relatively coarse particles in the atmosphere. Rayleigh has shown that dust-free air and other gases can scatter light, and in every case, the scattered light is blue.

It thus appears that it is unnecessary to postulate an atmosphere containing dust in order to account for the blue of the sky.

The sunrise and sunset colours are due to absorption of light. On account of the deeper layers of air through which the sun's rays have to pass slantwise at sunrise and sunset, the extent to which the blue light is scattered reaches a maximum. The residual red and orange light illuminating atmospheric haze and clouds provides the basis for the glorious tints so commonly observed.

Blue Eyes.—The structural blue colour of the eye is again due to light scattering by means of finely divided particles suspended in the liquid medium of the iris. The structural blue is modified, in the cases of green, brown and black eyes, by the coloured layer before the iris, namely, the uvea, which also acts in preventing the red blood from showing and cutting down

reflection from the back of the eye (cf. Bancroft, " Colour of Colloids," *J. Phys. Chem.*, 1919, p. 154).

Iridescent Colours of Birds' Feathers.—The brilliant, flashing, metallic, iridescent colours of the tail feathers of a peacock or the throat feathers of a humming bird are subjective structural colours (*v. supra*) and are caused by the thin laminæ in the barbules of the feathers. No bright pigment can be extracted from these feathers, nor is the colour effect destroyed by bleaching materials. The effects vary with the angle of incidence of the light to a greater extent than can be accounted for on the theory of selective reflection. The iridescent colours are true interference colours akin to the coloured " Newton's rings," as they are visible by reflected light and not by transmitted light. Indeed, as Bancroft says, the beautiful tail feathers of the peacock, viewed by transmitted light, show no more signs of colour than do the feathers of a crow.

An examination of the structure of iridescent feathers of many birds shows that the barbules—wherein the colours originate—consist of a core of fibrous or granular matter, two microns in thickness, covered by three thin laminæ apparently in contact, each 0·4 micron thick. A final thin plate or laminated structure completes the barbule, which acts as a multiple thin film. A dark brown pigment provides a background for the interference colours, and aids the production of the flashing metallic lustre, but the colour effects remain until almost the whole of this pigment has been removed and can then be observed under the microscope.

The curvature of the barbules is the factor determining the final beauty and delicate blendings of hues in the iridescent feather. This is due to the different angles at which different parts of the barbule are viewed and, as noted above, the interference colours change with the changing angle of incidence of the light. Plain thin films cannot create the soft blended hues obtaining in the feathers and built up in the curved laminated structure.

The differences of colour and gradations of effect upon a single feather are due, in addition, to slight variations in the thickness of the colour-producing laminæ. A surprisingly small difference in thickness, however, will cause a marked alteration in the interference colours, and it is marvellous, as Bancroft says, that the same general types of coloured feathers are produced generation after generation with such exactitude, when a relatively minute change in the thickness of the microscopic films would entirely alter the general appearance.

COAL-TAR COLOURS

By E. Arthur Bearder, M.Sc.

Colour has a very definite place in the scheme of the Universe. The human race has from the earliest times adorned itself with colours as bright as were available under the particular exigencies of time and place. The savages decorated their bodies with pigments derived from the roots, flowers, and fruits of trees and plants, as though in protest against an advantage vouchsafed to lower forms of life and in determination to increase, by the application of art, their attractiveness. More than 5000 years ago indigo, extracted from a plant cultivated in the valley of the Nile, was employed by the ancient Egyptians for dyeing their garments, whilst the famous Tyrian purple—or "Purple of Kings," now known to have been closely related chemically to indigo—with which the toga of the Roman emperors was dyed, was extracted at great cost from a species of sea-snail found in the Mediterranean. Down through the ages it has been the custom of civilised and uncivilised mankind to have recourse to colour as a means of personal embellishment. Accounts of discoveries recently made in the tomb of Tutankhamen tell us of the exquisite beauty of the decorative colouring executed by the craftsmen of the period in which the Pharaohs lived.

In those days thousands of years ago, and indeed right up to the middle of the nineteenth century, the colouring matters employed were all of natural origin and, although the processes by which they were applied were often extremely long and tedious and very little understood, an extraordinarily wide range of shades could be obtained by the skilled dyer, many being of great beauty and some possessing durability comparable with the best obtainable by the modern dyer of the present time.

The tinctorial art of to-day is very different from that of the ancients, and stands upon an entirely different structure, the foundation stone of which was laid in the year 1856 by the distinguished English chemist William Henry Perkin, who, in seeking for a method of synthesising quinine, discovered what proved to be the key which subsequently unlocked the door of a veritable Aladdin's cave whence chemical excavators have unearthed one by one over a thousand valuable coal-tar dyes.

Coal-tar colours, or aniline dyes as they are frequently and less accurately designated, are synthetic organic compounds, not extracted, but derived by a series of chemical reactions from the oily fluid, coal-tar, obtained during the destructive distillation of coal in the manufacture of coal-gas. Prior to Perkin's discovery of the first synthetic dyestuff, mauve, coal-tar was a waste product and a burden to the gas-maker.

By process of distillation this substance is separated into a number of components, benzol, toluol, xylol, phenol, naphthalene, anthracene, etc., which serve as the raw materials for the manufacture of the vast number of dyestuffs of commerce, and a residue of pitch.

The general scheme of dyestuff synthesis is represented by:

Raw Product → Intermediate → Dyestuff.

Immediately a raw product has undergone any chemical change in the direction of dyestuff, the body resulting from that change is an "intermediate," and all the succeeding stages are "intermediates" right up to the final point where the product is an intensely coloured body which has tinctorial affinities rendering it a dyestuff. The intermediate phase may be simple as, for example: Benzol → nitrobenzol → aniline → diazobenzene → (+ Betanaphthol) → Sudan I or it may be highly complex as in the case of Indigo: Naphthalene → phthalic

anhydride → phthalimide → anthranilic acid → phenylglycine-*o*-carboxylic acid → indoxyl carboxylic acid → Indigo.

It will be obvious, then, that it is the intermediate products which are the important factor in the scheme. The conversion of the final intermediate into the dyestuff is comparatively simple. It follows that successful dyestuff manufacture is, in reality, successful intermediate manufacture, and the importance of this realisation will be appreciated when it is borne in mind that each stage demands the highest efficiency in the way of economy and purity of production.

The bulk of the operations consists in the application of such standard reactions as nitration, reduction, sulphonation, alkali fusion, halogenation, alkylation, acylation, and diazotisation and coupling. The conditions appropriate to any particular set of circumstances are first determined in the works laboratory, after which the chemist in co-operation with the engineer effects the transference to the factory *via* a semi-works plant stage.

It does not fall within the scope of this article to discuss in any detail the different chemical classifications or the application categories of the coal-tar dyes. It will be sufficient to indicate that the immediate aim of the manufacturer of these commodities is to improve, simplify, and perfect the processes whereby raw materials are converted into dyestuffs, just as his ultimate purpose is to increase his range with a view to supply the consumer with the brightest, purest, and fastest colours in accordance with the increasing demands of an enlightened and critical public.

By the application of certain principles, then, to the various raw products derived from coal-tar, chemists in England and abroad, inspired by the first-fruit of Perkin's work, gradually evolved a range of dyes and thus commenced a revolution in dyeing methods, for the new products required different methods of application from those hitherto employed with the natural colouring matters. During the first decade of activity in coal-tar dyestuffs a discovery was made which has been responsible for the production of more individual dyestuffs than any other single chemical reaction. I refer to the diazo-reaction and the dyes of the azo-class.

The year 1868 stands out as a milestone on the road of organic chemical discoveries. The increasing tendency for more or less empirical research to give way to ordered and well-directed scientific syntheses found its reward in the synthesis of alizarin from anthracene, which had hitherto been obtained exclusively from the root of the madder plant, a substance the use of which for the production of Turkey Red was of great antiquity. This was the first instance of the synthetic imitation of a colouring matter occurring in nature. At the present time, the whole of the vast amount of alizarin used for the colouring of textiles is of synthetic origin, as also is the whole of this substance used in the manufacture of its numerous derivatives, which, like the parent substance, find a wide employment in dyeing and printing by virtue of the excellent properties of fastness possessed by them.

The second brilliant synthesis of a naturally occurring dyestuff was that of indigo some twelve years later. However, the process then worked out was not found capable of successful industrial application, and it was nearly twenty years later that a successful manufacturing process for synthetic indigo was finally perfected. It has been computed that the total monetary cost of establishing this manufacture was not less than £1,000,000. As in the case of alizarin, so with indigo, the synthetic gradually replaced the natural product in the dyehouses of the world, until at the present time only a small fraction of the total indigo consumed originates from the leaves of plants.

It is interesting to reflect upon the effect, quite apart from the immediate object in view, of the accumulation of scientific effort put into the researches on synthetic indigo. Not unnaturally, improvements upon the older methods of dyeing came to light, the most radical and far-reaching being the replacement of the antiquated " fermentation vat " by the simpler, more scientific, and more easily controlled " hydrosulphite vat." Incidentally, this change-over created a demand for the hitherto commercially unknown hydrosulphites, thus extending the scope of operations of the indigo manufacturer. Then the hydrosulphite-metal compounds and the related formaldehyde bodies were soon found to possess useful discharging properties, by reason of which they are to-day in great demand for stripping colours from dyed fabrics and have considerable application in fabric printing.

But perhaps the greatest benefit accruing from these researches has been the valuable knowledge acquired by the chemist which led to the discovery of the new and closely related colouring matters, known as the " indigoid " vat dyes, early in the twentieth century. A complete range of these colours of great beauty, possessing similar excellent properties of fastness and applied by the same method as indigo, had been evolved within a few years of the discovery of the first substituted indigo.

In spite of their good properties, however, the new additions to the indigo family are not, according to the high standard obtaining at the present time, in the first rank of durable colouring matters. Still, the range is constantly increasing and they find a vogue where either the very fastest results are not essential or where faster dyes cannot be satisfactorily applied.

At the beginning of the twentieth century the Alsatian chemist, René Bohn, discovered the first member of a new series of dyes derived from anthraquinone, to which the generic name of " Indanthrene " was given. By a curious coincidence, the first member, as in the case of the class just considered, was blue. This was soon followed up by a long range of derivatives and closely related products of the most varied hues and possessing properties of fastness unparalleled in any other series. The colours of this class are the most permanent at the disposal of the cotton dyer and calico printer.

It is an unfortunate fact that no single dyestuff has yet been found which combines all the best qualities and none of the disadvantages, and even these very admirable indanthrenes are not without drawbacks, which in some members take the form of comparative fugitiveness to light or bleaching or some other agency, whilst most of them are limited in their sphere of applicability. As a class they are not suitable for the colouring of animal fibres, though some individuals are capable of being used on silk, and there are indications that a method may ultimately be evolved which will render the series, as a whole, more generally applicable to the animal fibres.

Since the birth of the first coal-tar colour, a very fugitive dye, the aim of the dye-maker has been threefold, namely, extension of range, attainment of superlative fastness, and simplicity of application. The two latter characteristics do not usually go hand in hand, and hence fastness is often sacrificed to ease of application, which, together with the consideration of the more costly nature of the more durable products, largely accounts for the continued existence of a very large number of the older dyes of indifferent fastness. On the other hand, the very severe treatment to which coloured textile fabrics are in modern times subjected renders it imperative that they should be dyed or printed with dyes possessing the maximum durability possible in the circumstances obtaining. For instance, an expensive suiting or costume cloth to be worn in the full blast of tropical sunlight would require to be dyed with a dyestuff pre-

eminently resistant to the action of light. On the other hand, an evening gown would not demand such a quality in the colour used, which would be selected rather with a view to beauty of shade under artificial lighting conditions.

The importance of the coal-tar colour industry may be judged from the enormous number of fields in which there is a demand for its products. Undoubtedly the greatest consumption is in the textile industries, but nevertheless they have a very wide application for non-textile purposes. We have only to look around and take stock of the objects of everyday life surrounding us—our clothing, our foot-wear, our houses, and all the manifold articles such as carpets, curtains, furniture coverings, wall-papers, and numberless other things—in order to realise how much the coloured objects with which we are familiar owe their attractiveness and value to the coal-tar colours. Even the food we eat and the liquors we drink do not escape the influence of these products of the distillation of coal, which find their way into innumerable edible products.

There is one aspect of the importance of the industry which is deserving of mention. A few years ago the manufacture of artificial silk from cellulose acetate became a commercial proposition and its production on an industrial scale commenced. Very grave obstacles were encountered, however, which were gradually overcome and ultimately an excellent saleable material was evolved. It was then found that, unlike the other varieties of artificial silk, this new one was not susceptible to the usual dyeing processes and, indeed, that it could not be dyed by any known process so as to yield shades of a useful degree of fastness. Without a suitable method of dyeing it was clear that the new fibre could have but a very limited utility, and consequently a great deal of attention was directed to the problem with the result that very praiseworthy progress has been made. If the problem has not yet been completely solved it is at least now possible to dye cellulose acetate silk in practically any hue required, and there is little danger of the young industry being stunted from difficulties in this direction.

The demand for colour has, then, become very great indeed, and in consequence the colour industry has grown to colossal dimensions. Its growth from infancy may well be described as a romance. The first coal-tar colour factory was erected at Greenford Green, near Harrow, in the year 1857, and of this works the present British Alizarine Company is the lineal descendant. Within a short space of time the industry got a foothold in Germany, where it developed with remarkable rapidity, never looking back and always receiving powerful financial and State support until, at the time of the outbreak of the Great War, it had become one of the richest enterprises in the world with ramifications reaching into every nook and corner of commerce. Contrast the state of affairs in England. Here, after a short life of brilliant prosperity, the industry began to flag before it had arrived at full maturity, and soon its prospects were blighted by the keen and merciless competition from Germany, who, having once attained a position of domination and realising the enormous power of the instrument in her hands for commercial progress, for scientific development, and for the general furthering of her national weal, spared no effort to prevent the recovery in the country of its birth of the colour industry. It has often been stated that the industry was stolen from us by the people of the Rhineland, but I imagine that is not the view of the thoughtful man. I would rather say that the failure of the dye industry to continue to expand in this country was due to lack of vision on the part of those with whom the matter rested and perhaps also, in a lesser degree, to the Englishman's natural love of adventure and research for its own sake. The German, always clever at exploiting the brains of others, saw the splendid opportunity that we were letting pass and cannot be blamed if he seized his chance. Howbeit, the result was deplorable for us, as the

events of the past decade have amply demonstrated. At the end of the year 1913 the colour manufacturing industry remaining in England was but a fraction of the volume of that of Germany, although such products as were being made were of good quality.

Let us examine, for a moment, the German coal-tar colour industry at the time of the outbreak of the War. Germany was supplied from within her own boundaries with all the essential raw materials: coal, metals, acids, alkalis, chlorine, bromine, etc., and was independent of outside sources of supply. She had Government support in all her operations as well as all the assistance that her financial magnates were able to give. Internal co-operation between the various firms was very close indeed, culminating in the formation of the "Interessen-Gemeinschaft," which embraced the whole of the German firms of any importance. By this arrangement economy of manufacture was secured, over-lapping of processes avoided, knowledge pooled, and the well-being of the participants in every possible way safeguarded. Possessing enormous resources and embracing every branch of the chemical and allied industries, the "I.G." became one of the most formidable combines the world has ever seen, and under its powerful influence the German colour industry flourished and attained the great position which it holds in the dye-making world to-day.

I have already endeavoured to illustrate the importance of the industry in relation to the present-day demand for dyestuffs. Its importance does not stop there, however. A successful colour industry depends primarily upon chemical knowledge acquired through research. This basic fact was early recognised, and each of the German factories became veritable training-grounds for research chemists, and were fed from the laboratories of the Universities, whence flowed a constant stream of young graduates, full of enthusiasm and eager to win the reward forthcoming to the successful research worker. This demand for young men with chemical training kept the Universities well stocked with students and thus the interest in chemical science was maintained at a high pitch and the nation generally benefited. For not every chemist trained in organic chemical research ultimately found his way into a colour factory, but many sought careers in other branches of industry in which the splendid training which they had received could be turned to good account. And the march of civilisation goes hand in hand with the progress of science—chemical science in particular.

To attempt to refer, in a limited survey, to all the ramifications which give to the coal-tar colour industry its supreme importance would be vain. There are, however, one or two phases which may be considered. Not the least of the many factors contributing to the favourable position achieved by the German firms has been the careful attention given to by-products, the recovery and conversion of which into useful commercial commodities, such as pharmaceutical products, photographic chemicals, etc., has had a profoundly favourable effect upon the conduct of the parent industry. Then, again, the fixation of atmospheric nitrogen was one of the most revolutionary achievements of modern science. To appreciate its significance, one has only to reflect upon the enormous advantages to agricultural interests of a supply of nitrogenous products prepared direct, by chemical means, from the nitrogen of the air. The colossal importance in the manufacture of munitions of war has been very clearly and forcibly demonstrated. Finally, the ready convertibility of dye-manufacturing plant from peace-time to war-time purposes is worthy of the most serious consideration.

Notwithstanding Germany's predominance, the dye-makers of that country were not our only pre-war competitors. Switzerland had built up a very considerable coal-tar colour industry, and her four principal firms, although small in comparison with those of her neighbour,

functioned independently and successfully manufactured a considerable range of dyestuffs, including a number of excellent specialities. Her industry was modelled largely upon the lines of the German, upon which, however, as upon England, she was dependent for supplies of raw materials, being deficient in natural resources. During the War, Switzerland was enabled greatly to improve her position in the dye-making world, owing to the impetus given by the deflection of business previously executed by the German concerns. The three larger firms are now closely associated in a Community of Interests which controls branch works at Clayton, near Manchester, and Cincinnati, U.S.A. The largest of the Swiss concerns, the Society of Chemical Industry, also has factories at St. Fons (France), Pabianice (Poland), and Moscow.

The greatest upheaval the dyestuffs industry has known since its commencement occurred in 1914. If we recall the circumstances in which the outbreak of war in August of that year found us, what do we see? For thirty or forty years Great Britain's source of supply of the dyestuffs essential for the maintenance of her great textile and other consuming industries has been mainly Germany, and to a much smaller extent Switzerland. The value of the textiles alone runs into well over £200,000,000 per annum and the main source of supply is suddenly cut off, whilst barely 10 per cent. of our needs are provided for by our own colour works. The position strikes a note of grave alarm, and we begin to realise the folly of having allowed ourselves to be almost completely dependent upon a foreign country for products so vital to us and to the continuance of one of our staple trades, and we look around for some means of retrieving the position. Everywhere we are confronted with obstacles. A stupendous war is raging and our War Department is in need of every available chemical plant capable of producing munitions of war and the drugs and antiseptics demanded by the medical services for the treatment of the wounded. Our organic chemical plants, including the well-adapted dye plants, are thus virtually pressed into the service of the State. But the demands of this service include a big and continuous supply of dyes—for our armies and those of our Allies have to be clothed and their uniforms need to be appropriately dyed. And so, after a long period of desultory working, our dye factories once again assume an aspect of vitality and extend their production.

At first this increased production was chiefly to cope with the enormous demands of the Government for khaki, blue, and field-grey, but in course of time it was possible to turn attention to dyestuffs for general use. Before the end of 1915 it could be said that danger of disaster from dyestuff famine had been averted. It is true that the dyeing industry was still severely handicapped through inability to obtain supplies of the same comprehensive range of colours to which it had become accustomed in 1914, and the fastest types were almost entirely lacking. For it must be remembered that dyers had had at their disposal over a thousand distinct types of foreign colours—a convenient, but not altogether essential, state of affairs. Even this temporary dark cloud had its silver lining, in that the dye-user, for so many years spoon-fed by the pushing, ubiquitous and ever obliging technical staffs attached to the colourist departments of the Continental firms, instead of appealing in his slightest difficulty to his accustomed source of aid, was compelled to rely upon his own efforts. In so doing he inevitably improved his knowledge of the application of the limited range of products to which he was now confined. The greatest credit is due to the resource and skill shown by the dyer thus placed on his mettle during the period of restriction.

Moreover, the difficulties encountered created a demand for tinctorial chemists, and very soon the supply of young men trained in those of our Universities and Technical Colleges which included tinctorial chemistry in their curricula became totally inadequate. It has often been alleged that, as a nation, we are indifferent to chemical research, and it is no doubt perfectly

true that we have but imperfectly realised its value and that we have not pursued it with sufficient vigour. But, however that may be, it would be entirely erroneous to suggest that dyestuff research in this country, at all events academic research, had ever been completely neglected. Its failure to progress at a sufficiently rapid rate has been due to causes which will, I think, be obvious from my previous remarks. Outside the teaching or consulting professions there was very little in the way of a career for our young graduate research chemists, and it is not to be wondered at that the laboratories of the Universities did not attract more young men of ability.

That we were able, at a critical period, to tackle the problem of dye manufacture and achieve a great measure of success was largely due to the fact that we had at our disposal a number—a very limited number—of first-class chemists who were not only well trained in organic chemical research but had also had at least a few years of experience prior to the War in technical dyestuff research and in works processes in such colour factories as we possessed. These men formed the nucleus of the now very considerable staffs responsible for the scientific and technical sides of our present-day factories. The crying need for chemists had the same effect in this country as had been experienced in Germany throughout the life of the industry. Our youths with an inclination towards chemical science saw the possibility of a career, and flocked to the Universities, which, in consequence, have been at some periods taxed to the utmost limit of their accommodation. The influx is still maintained, but it is doubtful whether all these men will eventually find their way into the special branch of chemical industry which is admittedly the richest training-ground for the organic chemist and attracted them to the career upon which they set out. Whatever their ultimate destination, however, it is certain that in whichever branch they find themselves the industry will be enriched by the application of their training and knowledge. To a great writer has been attributed the saying, " There is nothing more desirable in life than to be wise at a great moment." The present is, surely, a great moment to our industrialists. It is to be hoped that they will not fail to show their wisdom by securing the continuation of the great industry which will ensure to the organic chemist a promising career.

During the boom years immediately following the Armistice the tangible result of the strenuous efforts of the British dye-makers was that our manufacturers were able to take advantage of the world's scarcity of textiles. At that period, encouraged by the success of existing concerns, more and more firms entered the arena of coal-tar colour making and with considerable financial advantage to themselves. Outside Great Britain, and advancing on similar lines, America was pushing ahead, and to-day her enterprise has grown to imposing dimensions. France is likewise in the field and now claims to be in a position to supply the bulk of her own requirements which, however, are not large.

The unprecedented prosperity enjoyed by Great Britain's dyestuff industry for a period of two years suffered a reverse when, towards the end of 1920, the trade slump fell upon the country. The condition was aggravated by a number of circumstances: the revival of the German production, the importation of German dyes by way of reparations, the temporary removal of all protection from the home producers by the Sankey judgment, and the rapid external depreciation of the German mark.

The immediate effect of the Sankey judgment, declaring illegal the Order in Council prohibiting the importation of foreign dyes, was the rushing into the country of vast quantities of these commodities. Foreseeing disaster to the domestic dye industry, our legislators passed, in December, 1920, an Act of Parliament known as the Dyestuffs Import Regulation Act, which

decreed that no synthetic organic dyestuff or intermediate product should be permitted to enter the country except under licence. The administration of this Act is in the hands of the Dyestuffs Advisory Licensing Committee of the Board of Trade, composed of representatives of the dye-using and dye-manufacturing interests in the country together with independent members, one of whom serves as chairman. The Committee is informed on technical matters by two technical advisers, one appointed by the dye-users and one by the dye-makers. In addition to this Committee, the President of the Board of Trade has appointed a somewhat similar Committee, but representative of rather wider interests, known as the Dyestuffs Industry Development Committee, whose function is to report upon the progress of the industry and to make recommendations with regard to its advancement.

Having traced the course of evolution of the coal-tar dye industry, its specific importance in relation to textiles, its bearing upon education, its general value to civilisation, and its revival in the country of its origin, we may appropriately conclude with a brief review of its position in Great Britain in this year 1924.

At the present time, there are over twenty firms manufacturing, in all their stages, from British raw materials, dyestuffs representing a total capacity considerably in excess of the normal demands of the home market and capable of supplying at least 80 per cent. of the requirements of the domestic textile and other colour-consuming industries. The fact that in 1913 the total production of the half-dozen firms then existing was not more than about one-tenth of that of the present time, and that the bulk of the colours was made from imported intermediates, indicates the extent of the progress made during the last ten years. Many of the larger concerns make their own intermediates, whilst outside the dye-makers there are a number of firms specialising in the manufacture of these products. Other chemicals of vital importance to the industry, such as chlorine, phosgene, oleum, antimony pentachloride, anhydrous aluminium chloride, sulphuryl chloride, thionyl chloride, acetic anhydride, etc., are being manufactured and are available in adequate supply.

Although the different firms function independently and are not associated in the commercial sense, they are combined together in common interest in membership of the Association of British Chemical Manufacturers, which embraces, in different groups, all branches of the chemical industry. The formation of the Association in 1916 marked the beginning of organised co-operation between the chemical interests in the country. During the past few difficult years this organisation has amply demonstrated its utility and value, particularly in reference to the sections either remotely or directly concerned with the manufacture of coal-tar colours.

SYNTHESES IN THE TERPENE SERIES

By G. G. HENDERSON, F.R.S., and ALEXANDER ROBERTSON, M.A.

WHEN the saps and tissues of certain plants (such as pines, lemons, thyme, etc.) are distilled, the distillates are found to contain, among others, substances known as *Essential Oils*, which consist chiefly of hydrocarbons of the general formula $(C_5H_8)_n$ and their oxygen derivatives, *e.g.* camphor. These constituents of the crude materials have been recognised in the course of the development of the natural sciences and with improvements in technology have been gradually prepared in a purer condition. The essential oils along with other natural products have from early times ministered to the needs of man and have therefore been appreciated by him in a special degree. As a natural consequence of this, they have been an influential factor in the commercial intercourse of nations; and in modern times the isolation and utilisation of these substances form the basis of a large and ever-growing branch of chemical industry.

The hydrocarbons which are found in the various essential oils are called Terpenes, and may be classified as follows:

1. Hemi-terpenes, C_5H_8: *e.g.* Isoprene.
2. Terpenes proper, $C_{10}H_{16}$:
   - (*a*) Aliphatic: *e.g.* Oxygen derivative Citronellal, $C_{10}H_{18}O$.
   - (*b*) Monocyclic: *e.g.* Limonene.
   - (*c*) Dicyclic: *e.g.* Pinene.
   - (*d*) Tricyclic: *e.g.* Tricyclene.
3. Sesquiterpenes, $C_{15}H_{24}$: *e.g.* Caryophyllene.
4. Polyterpenes, $(C_5H_8)_n$.

The hemi-terpene, isoprene, which has not so far been found in nature but may be obtained by the destructive distillation of rubber, may be regarded as the parent substance, and all terpenes would seem to be condensation products of two or more molecules of isoprene.

The terpenes generally are colourless liquids with a somewhat pleasant odour which boil without decomposition and are volatile in steam. Some of them show optical rotation, while others do not. Occurring along with the terpene hydrocarbons—though not always in the same oil—are their oxygen derivatives—alcohols, aldehydes, and ketones.

The investigation of the chemical properties and constitution of these interesting substances (chiefly by analytical methods) has occupied many of the leading chemists in different countries for a long time. The work has been beset with great difficulties, which arise chiefly from the ease with which these bodies undergo isomeric change. In many cases, the formulæ given to the individual hydrocarbons were more or less tentative, and it was not until they had been produced synthetically that their constitution was definitely established.

It would be impossible in a summary of this kind to attempt to give even a very brief description of the work on the terpenes and their derivatives which has been carried out by British chemists. For this reason, we shall confine ourselves to the synthetic side of the work, and even then it will only be possible to give examples, more or less typical, of the syntheses which have been carried out by different investigators in British laboratories.

We may note in passing that one of the earliest attempts at a natural classification of the

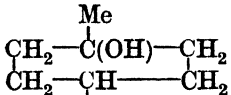
terpenes was that of the English chemist Gladstone, but it was not until the introduction of nitrosyl chloride as a terpene reagent by Tilden that a decided advance in the analytical method was made.

If we consider rubber as a member of the class of polyterpenes, then the first real synthesis of a terpene was carried out by Tilden in 1882, when he succeeded in causing isoprene to polymerise into rubber. Up to 1900, very little success in this country or elsewhere had been achieved on the synthetic side. In that year, W. H. Perkin, jun., and his collaborators started a long series of explorations in this practically virgin field of research, and in 1904 published an account of the synthesis of dipentene, the inactive form of limonene. This was the first recorded synthesis of a naturally occurring terpene hydrocarbon, and the initial success was rapidly followed by others.

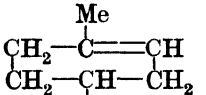
Perkin's Syntheses of Terpenes

Synthesis of Dipentene (*dl*-Limonene)

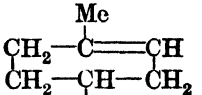
Dipentene, which is the *dl* form of limonene, occurs widely, along with its derivatives terpineol and terpin. From analytical considerations, Wagner had been led to give to them the following formulæ:



Terpin.



Terpineol.



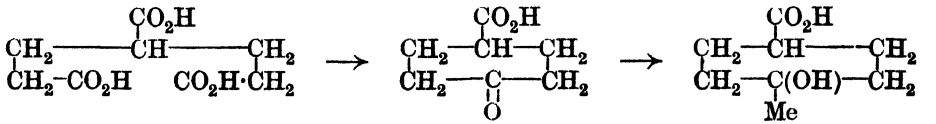
Dipentene.

These substances are derivatives of 1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid; and it was the problem of the synthesis of this acid which held up the work for four years.

When the sodium derivative of ethyl cyanoacetate and ethyl β-iodopropionate are allowed to interact at the ordinary temperature, ethyl γ-cyanopentane-$\alpha\gamma\varepsilon$-tricarboxylate is formed:

$$2CO_2Et\cdot CH_2\cdot CH_2I + 2CO_2Et\cdot CHNa\cdot CN = CO_2Et\cdot C\cdot(CN)(CH_2\cdot CH_2\cdot CO_2Et)_2 + CO_2Et\cdot CH_2\cdot CN + 2NaI.$$

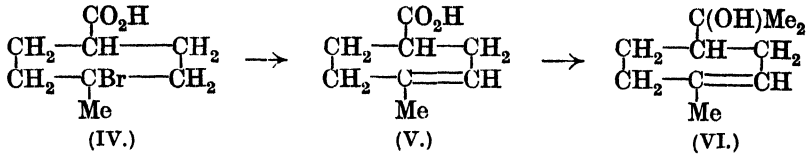
The acid on hydrolysis yields pentane-$\alpha\gamma\varepsilon$-tricarboxylic acid (I), and on heating the sodium salt of this acid in acetic anhydride, carbon dioxide and water are eliminated with the formation of *cyclo*hexanone carboxylic acid (II). When the ethyl ester of this acid is treated with magnesium methyl iodide 1-methyl*cyclo*hexanol-4-carboxylic acid (III) is formed.



(I.) (II.) (III.)

The acid on treatment with hydrobromic acid gives the corresponding bromo-acid (IV), and this on decomposition with alkali gives 1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid (V). The

ester of this acid, when treated with magnesium methyl iodide, and subsequently with water, gives an almost quantitative yield of terpineol (VI).



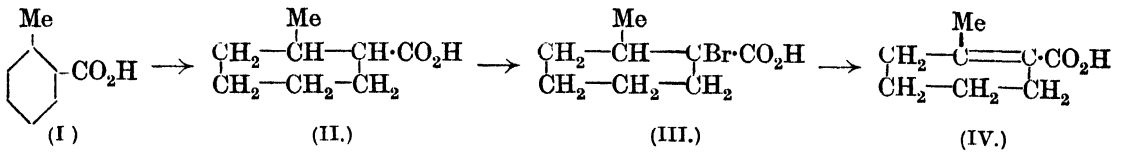
(IV.) (V.) (VI.)

When the synthetic terpineol was dehydrated with $KHSO_4$, dipentene was formed, and this hydrocarbon was found to be identical in all respects with that which occurs in some essential oils. The synthetic terpineol when digested with dilute sulphuric acid was converted into terpin.

These synthetic products are necessarily optically inactive. By resolution of the *dl*-1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid with the aid of its brucine salts, an active terpineol was prepared, but this active terpineol could not be dehydrated to give an active dipentene (or limonene), as racemisation took place even in the cold in presence of a dehydrating reagent.

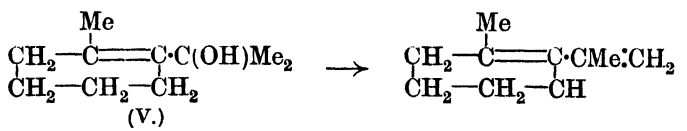
Synthesis of an Orthomenthadiene.—As an example of a synthesis in the ortho-series of menthadienes, we may take that of $\Delta^{1:8(9)}$-*o*-menthadiene.

Ortho-toluic acid (I) on reduction with sodium and amyl alcohol was converted into 1-methyl-*cyclo*hexane-2-carboxylic acid (II), which on treatment with bromine gives the bromo-acid (III). This bromo-acid on treatment with alkali was converted by loss of hydrobromic acid into 1-methyl-Δ^1-*cyclo*hexene-2-carboxylic acid (IV).



(I) (II.) (III.) (IV.)

The ethyl ester of this unsaturated acid, when treated with two molecules of magnesium methyl iodide, yielded Δ^1-*o*-menthen-8-ol (V), from which $\Delta^{1:8(9)}$ *o*-menthadiene (VI) was obtained by dehydration.



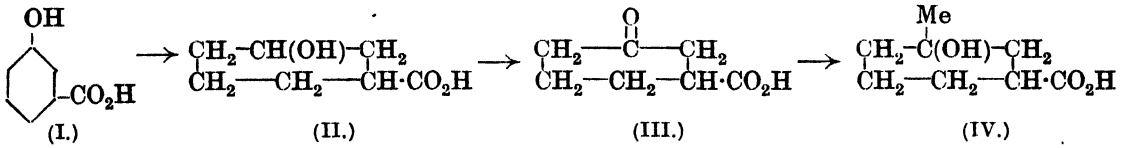
(V.)

The hydrocarbon is a typical example of a terpene with two conjugated double bonds. This structure causes an increase in the refractive index over the calculated theoretical value and a rise in boiling point. Such hydrocarbons unite with only one molecule of halogens and halogen acids.

Synthesis of Carvestrene and Sylvestrene.—Sylvestrene, which occurs in Swedish oil of turpentine, may be regarded as a derivative of *m*-cymene. It is the optically active form of carvestrene, which occupies the same position in the meta-series of menthadienes as dipentene does in the para-series.

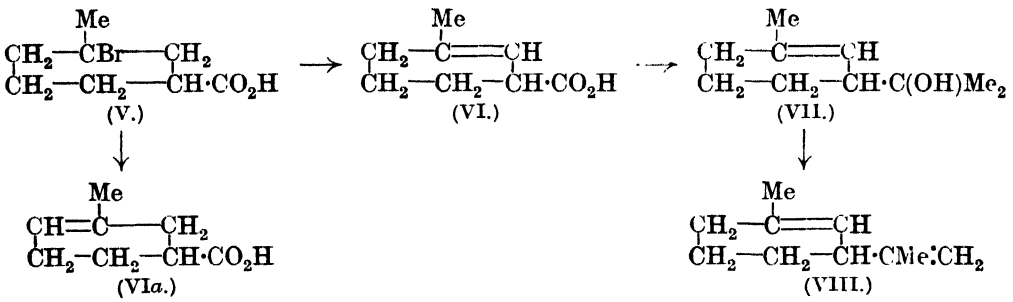
Perkin and his collaborators successfully tackled the problem of the synthesis of this hydro-

carbon, taking as the starting point *m*-hydroxybenzoic acid. The acid (I) on reduction with sodium and alcohol was converted into *cyclo*hexanol-3-carboxylic acid (II), which was then oxidised with chromic acid to the corresponding *cyclo*hexanone acid (III). The ethyl ester of this acid, on treatment with magnesium methyl iodide, gave 1-methyl*cyclo*hexan-1-ol-3-carboxylic acid (IV).



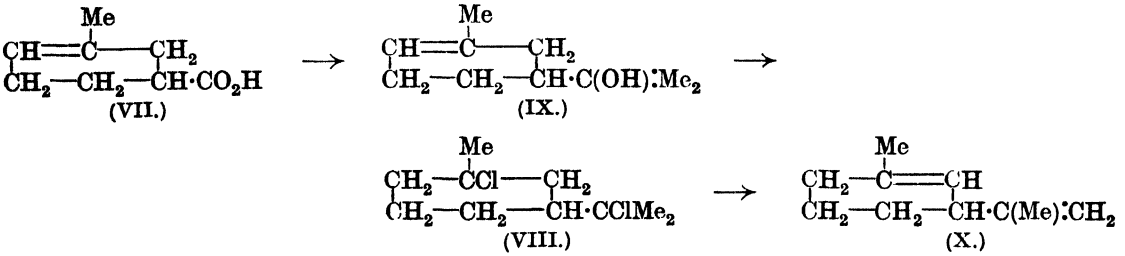
(I.) (II.) (III.) (IV.)

The acid (IV), on treatment with hydrobromic acid, was converted into the corresponding bromo-derivative (V), and the bromo-acid, when digested with pyridine, was decomposed, with the elimination of hydrobromic acid and the formation of 1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid (VI), along with small quantities of the Δ^6-acid (VI*a*). The ester of the acid (VI), when treated with magnesium methyl iodide, yielded dihydrocarvestrenol (VII), or Δ^1-*m*-menthen-8-ol, which, when heated with potassium hydrogen sulphate, was converted by loss of water into carvestrene (VIII).



(V.) (VI.) (VII.) (VIa.) (VIII.)

This synthetic carvestrene was found to give a dihydrochloride identical in all respects with the dihydrochloride of the naturally occurring substance.



(VII.) (IX.) (VIII.) (X.)

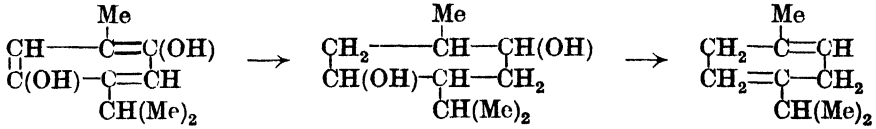
Sylvestrene, which is the dextro-isomer of carvestrene, was obtained by resolving the mixture of acids obtained from the decomposition of the 1-bromo-1-methyl-*cyclo*hexane-3-carboxylic acid (V), when a quantity of an acid, 1-methyl-Δ^6-*cyclo*hexenecarboxylic acid (VI*a*) was obtained which was dextrorotatory, $\alpha_D + 90°$. The ester of this acid on treatment with magnesium methyl iodide yielded *d*-dihydro*iso*sylvestrenol (IX), which, strange to say, was optically inactive. When treated with hydrochloric acid, however, this substance yielded an active

hydrochloride, sylvestrene hydrochloride (X), m. p. 72°, α_D + 22°, and this hydrochloride by elimination of hydrochloric acid with aniline was converted into sylvestrene, α_D + 66° (XI).

Henderson's Syntheses of Terpenes

A number of menthadienes with conjugated double bonds have also been synthesised by Henderson and his collaborators, but the methods adopted were different from those just described, as the following examples will show.

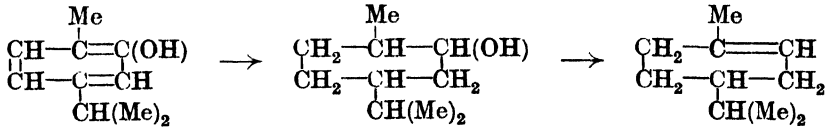
Synthesis of $\Delta^{1:4}$-p-*Menthadiene.*—The starting point of this synthesis was thymol, from which *o*-nitrosothymol was prepared. The nitrosothymol on reduction gave the corresponding amino-derivative, which was oxidised to thymoquinone, and this in turn on reduction with sulphurous acid yielded thymoquinol (I). This dihydric phenol was hydrogenated by the method of Sabatier and Senderens, and menthane-2 : 5-diol (II) was obtained. On digesting this glycol with potassium hydrogen sulphate, a hydrocarbon, $C_{10}H_{16}$, was obtained which is $\Delta^{1:4}$-*p*-menthadiene (III).



(I.) (II.) (III.)

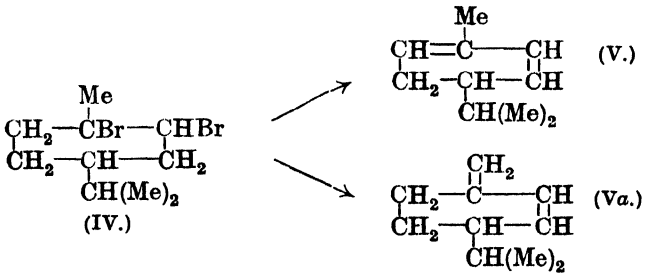
This hydrocarbon showed the normal physical and chemical properties of a terpene hydrocarbon; it formed additive derivatives and oxidised rapidly when exposed to the air.

Synthesis of a p-*menthadiene from hexahydrocarvacrol.*—Carvacrol (I) was converted into carvomenthol (II) by hydrogenation in the presence of finely-divided nickel by the Sabatier-Senderens method. The carvomenthol on heating with anhydrous oxalic acid was converted by the elimination of water into Δ^{1}-*p*-menthene (III).



(I.) (II.) (III.)

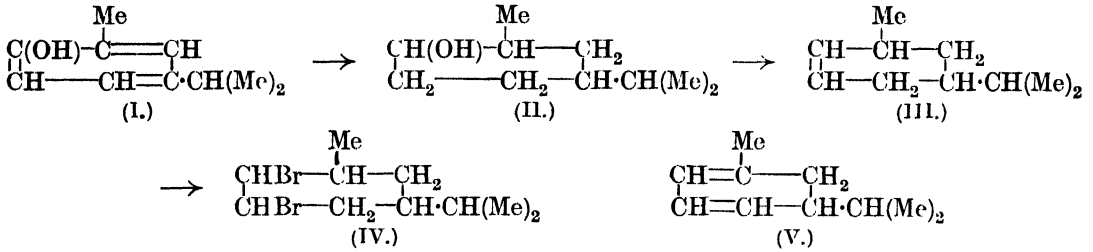
The menthene (III), when treated with one molecule of bromine, gave a dibromide (IV), and on heating this dibromide with alcoholic potassium hydroxide a *p*-menthadiene



was obtained. The hydrocarbon has conjugated double bonds and is probably $\Delta^{2:5}$-*p*-menthadiene (V).

This menthadiene should have been either α- or β-phellandrene (V*a*); the latter are easily characterised by their nitrites, but the synthetic hydrocarbon did not give a nitrite; hence it is assumed that the formation of the dibromide of the Δ^1-menthene must have been attended with intramolecular change.

Synthesis of m-*menthadiene.*—By the methods used by Perkin and his collaborators in their syntheses of the meta-menthadienes, only one double bond was formed in the ring structure. A synthesis was therefore carried out in order to obtain a *m*-derivative with two double bonds in the ring. *m-iso*Cymene was obtained by the action of phosphoric oxide on the ketone fenchone, and converted into *m-iso*cymene-6-sulphonic acid, which gave the corresponding phenol on fusion with alkali. The phenol (I) was hydrogenated in the presence of finely-divided nickel by the Sabatier-Senderens method, and yielded *m*-menthen-6-ol (II). This menthenol, when treated with anhydrous oxalic acid, passed with the elimination of water into 1-methyl-3-*iso*propyl-Δ^5-*cyclo*hexene (III). The unsaturated hydrocarbon, on treatment with bromine, gave the dibromide, 4 : 5-dibromo-1-methyl-3-*iso*propyl*cyclo*hexane (IV).

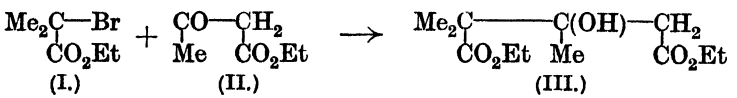


This dibromide when treated with alcoholic potash was found to yield 1-methyl-3-*iso*propyl-$\Delta^{4:6}$-*cyclo*hexadiene (V). The formula for this hydrocarbon was verified by various considerations, and the substance was found to be a *m*-menthadiene with two ethylenic linkages in a conjugated position in the ring system.

Perkin and Thorpe's Syntheses of Camphoric and Camphoronic Acids

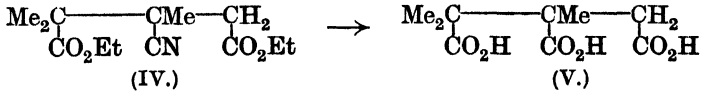
Among the oxygen derivatives of the terpenes, the ketone camphor has perhaps attracted more workers than any other, for, on account of its relationships to so many terpene compounds, the determination of its constitution was a matter of great importance. From this ketone a large number of degradation products have been obtained, amongst which are (*a*) camphoric acid and (*b*) camphoronic acid. Both of these have been synthesised by Perkin and Thorpe, and thus the constitution of camphor has been elucidated.

Synthesis of Camphoronic Acid.—By the action of zinc on a mixture of acetoacetic ester (I) and α-bromo*iso*butyric ester (II), β-hydroxy-trimethyl glutaric ester was obtained (III).



The hydroxyl group was then replaced by chlorine and the latter by cyanogen, when the

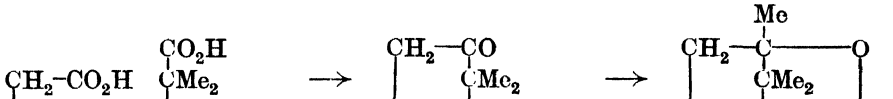
nitrile ester (IV) of camphoronic acid was produced. From this nitrile ester by hydrolysis, camphoronic acid (V) was obtained.



(IV.) (V.)

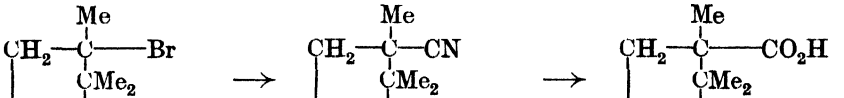
Synthesis of Camphoric Acid.—Camphoric acid is a direct oxidation product of camphor, and Haller in 1896 had shown that camphor could be obtained from the acid, but the difficulty was the synthesis of the acid itself. This was accomplished independently by Komppa in 1903 and by Perkin and Thorpe.

The latter workers started from αα-dimethylbutane-αβδ-tricarboxylic acid (I), the sodium salt of which when treated with acetic anhydride yielded a dimethyl*cyclo*pentanone carboxylic acid (II). The ester of this acid on treatment with magnesium methyl iodide was converted into α-campholactone (III).



(I.) (II.) (III.)

This lactone, by treatment with hydrobromic acid, yields a bromo-trimethyl*cyclo*pentanone-carboxylic acid (IV). The bromine atom is replaced by the cyanogen group by shaking with potassium cyanide and the nitrile (V) is obtained, which on hydrolysis yields camphoric acid (VI).



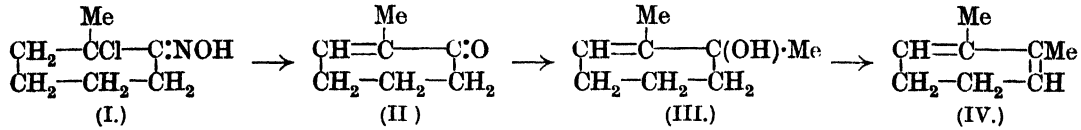
(IV.) (V.)

Haworth's Syntheses of Hydrocarbons related to Terpenes

The peculiar properties of the terpene hydrocarbons have led several investigators to prepare related hydrocarbons by synthetic methods and to compare their physical and chemical properties with those of the true terpene hydrocarbons. A number of such substances have been prepared at different times, and in many cases have been found to have similar properties to the terpenes. As an example of this type of synthetic work, we may note that of Haworth.

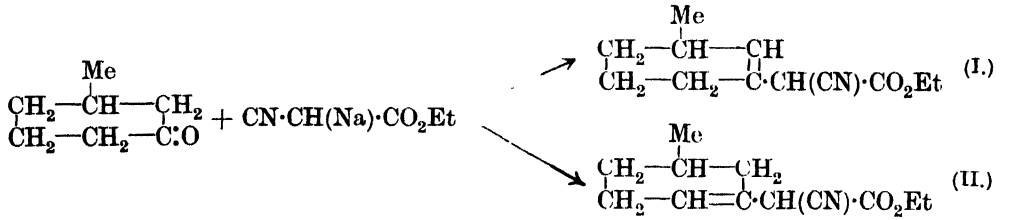
Synthesis of Cantharene, C_8H_{14}.—This hydrocarbon is a dihydro-*o*-xylene, and had been obtained by Piccard in his researches on cantharidene, though some doubt as to the purity of the hydrocarbon existed. Haworth succeeded in preparing the hydrocarbon in a pure state. By digesting the nitrosyl chloride of 1-methyl*cyclo*hexene (I) with anhydrous sodium acetate in glacial acetic acid the ketone 1-methyl-Δ^6-*cyclo*hexen-2-one (II) was obtained. This ketone on treatment with magnesium methyl iodide yielded 1 : 2-dimethyl-Δ^6-*cyclo*hexen-2-ol, or cantharenol (III). When this alcohol was dehydrated by heating with 8 % oxalic acid, the hydro-

carbon 1 : 2-dimethyl-$\Delta^{2:6}$-*cyclo*hexene (IV) was obtained. This hydrocarbon was found to be identical in every way with cantharene.



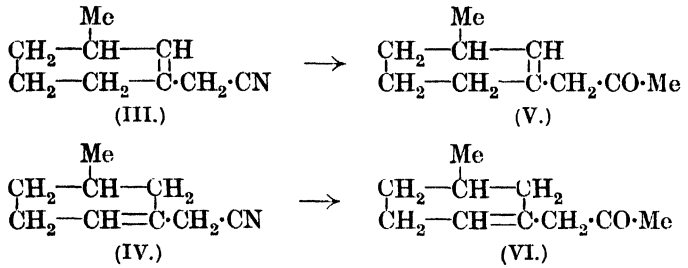
(I.) (II.) (III.) (IV.)

Synthesis of d-1-*Methyl*-3-*dimethylvinyl*-Δ^2-cyclo*hexene and* d-1-*Methyl*-3-*dimethylvinyl*-Δ^3-cyclo*hexene.*—These hydrocarbons are representative examples of terpene hydrocarbons, $C_{11}H_{18}$, with one carbon atom more than the naturally occurring products. Their synthesis was carried out as follows : d-1-methyl*cyclo*hexan-3-one was condensed with ethyl sodiocyanoacetate and gave rise to a mixture of two cyclic unsaturated esters (I) and (II) :



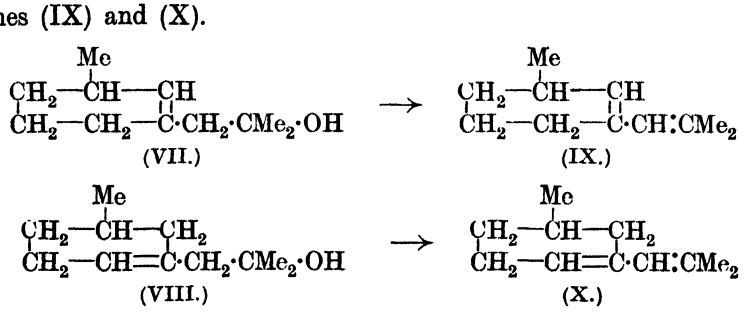
(I.) (II.)

By the distillation of the cyano-acids of these esters, carbon dioxide was eliminated and nitriles (III) and (IV) were formed. These nitriles were treated with magnesium methyl iodide under special conditions and a mixture of two ketones, (V) and (VI), was obtained, which were separated by aid of their semicarbazones.



(III.) (V.) (IV.) (VI.)

The ketones on treatment with magnesium methyl iodide yielded two carbinols, (VII) and (VIII), which when dehydrated gave two hydrocarbons—the Δ^2- and Δ^3-d-1-methyl-3-dimethylvinyl*cyclo*hexenes (IX) and (X).



(VII.) (IX.) (VIII.) (X.)

These hydrocarbons possess a system of two conjugated ethylenic linkages, and were found

to possess physical and chemical properties very similar to the true terpene hydrocarbons of this type.

Synthetic Rubber

Several colloidal substances similar in properties to natural rubber have been obtained by the polymerisation of certain hydrocarbons, particularly butadiene, $CH_2{:}CH{\cdot}CH{:}CH_2$, isoprene, $CH_2{:}C(CH_3){\cdot}CH{:}CH_2$, and some others. The reaction may take place spontaneously, in the cold or on heating, but is greatly accelerated by the presence of suitable catalysts. The rubbers so obtained, or at least some of them, are capable of being vulcanised like natural rubber.

In 1882, Tilden observed that isoprene is converted into rubber when brought into contact with nitrosyl chloride, and pointed out that if it were possible to obtain isoprene at a moderate cost, the synthetic production of rubber on the manufacturing scale could be accomplished. In 1892, he found that synthetic rubber, which he had obtained by the spontaneous polymerisation of isoprene, could be vulcanised. In 1910, Matthews observed that a tube in which isoprene had been sealed up along with some metallic sodium contained a solid mass of rubber. Further work showed that sodium is a catalytic reagent of the first importance for bringing about the polymerisation of butadiene and its homologues, and a patent for the preparation of synthetic rubber by this process was taken out.

When possible improvements in the production of natural rubber and difficulties which arise in practice in the manufacture of synthetic rubber of satisfactory quality are taken into account, it appears unlikely that the synthetic will be able to compete with the natural product as regards price. At the present time, the manufacture of synthetic rubber, which was carried on during the war, appears to have been abandoned.

The foregoing brief summary, in which, as previously stated, only typical examples can be given, may serve to indicate, to some extent at least, the activities of British chemists in this rather difficult field of investigation. Of the sesquiterpenes and polyterpenes, nothing definite can be said at present, as the work on these substances is only in the initial stages.

When we survey this field of synthetic organic chemistry, which deals with these plant products, it is impossible to overlook the fact that although many of these substances have been produced in the laboratory, the methods and reagents are entirely different from those employed by the living plant. We need only compare the physical conditions of temperature and pressure to see how far apart these methods really are. The plant produces these and other products from carbon dioxide, water, and nitrogen, but as to how such substances are produced we are almost entirely ignorant, and the same must be said of the function of these essential oils in the economy of the plant. Some maintain that they are the intermediate products, while others say that they are the waste products of plant metabolism. But these, at present, are little more than hypothetical opinions. Certain it is, however, that when the difficulties of the constitution and reactions of these substances have been cleared up, we have an ever-widening and still more interesting field ahead of us—the study of the formation and function of these substances in the plant itself.

THE ALKALOIDS

By T. A. Henry, D.Sc., and F. L. Pyman, F.R.S.

The first quarter of the twentieth century, to which we are making special reference, is the centenary of our knowledge of the alkaloids as chemical individuals, for it was during the first quarter of the nineteenth century that alkaloids were first isolated in a pure state from the plants in which they were contained. Thus, morphine was first isolated by Seguin in 1804, and after the recognition of its basic nature by Sertürner in 1817, other alkaloids were soon obtained in a pure state, for instance, strychnine by Pelletier and Caventou in 1817, and quinine by the same chemists in 1820. None of these three important alkaloids has been synthesised up to the present, and the constitution of quinine alone has been established. Several alternative formulæ for morphine are under discussion, whilst the constitution of strychnine is still a matter for speculation.

Amongst the many alkaloids first isolated in a pure state by British chemists are sparteine, the alkaloid of broom tops, isolated by Stenhouse (1852), hydrastine isolated by Perrins (1862), and the three most important alkaloids of ipecacuanha, emetine, cephaeline, and psychotrine, isolated by Paul and Cownley (1894).

A brief account of the part which British chemists have played in determining the constitutions of alkaloids and effecting their synthesis appears below. Before treating of special groups, however, reference will be made to two subjects of general alkaloidal interest. Dobbie, with his collaborators Lauder, Tinkler and Fox (1903–1914), has investigated the absorption spectra of a very large number of alkaloids, and established for those of known constitution the fact that the spectra are either identical with or very closely resemble the spectra of the unreduced part of their molecules. With the knowledge which has thus been accumulated, it has been found possible to gain evidence of the structure of other alkaloids of undetermined constitution by examining their absorption spectra.

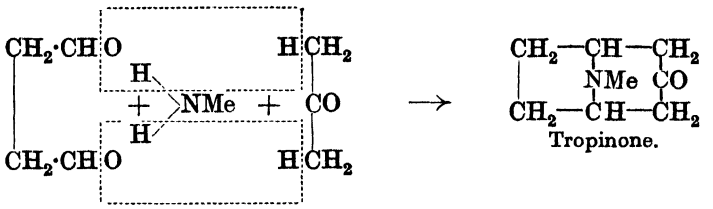
Chemists have speculated from time to time on the methods by which alkaloids are formed in plants, and made various suggestions as to the way in which individual bases are formed, but generally found it necessary to postulate that the plants made use of methods for which no analogy existed in laboratory practice. Robinson (1917) has developed a theory of the mechanism of the phyto-chemical synthesis of alkaloids, and has shown that the skeletons of alkaloids generally may be built up from amino-acids and derivatives of carbohydrates by postulating the linkage of carbon to carbon by two methods only, both of which readily take place under laboratory conditions, namely, aldol condensation and the similar condensation of carbinol-amines with substances containing the group ·CH·CO.

The Tropane Group includes three alkaloids of medicinal importance and many others. These three are atropine (*dl*-hyoscyamine), which has mydriatic properties, hyoscine, which is employed as a mental sedative, and cocaine, which has local anæsthetic properties.

Atropine, discovered by Mein in 1833, is the tropyl ester of tropine, and was recognised as a derivative of tropane by Willstätter in 1898, who effected the synthesis of tropine in 1901–1903 by a lengthy method starting from suberone. In 1917, Robinson devised a very simple and elegant synthesis of tropinone—which yields tropine and ψ-tropine on reduction—by the interaction of succindialdehyde, methylamine, and acetone (or calcium acetone-dicarboxylate) at the ordinary temperature, as shown on the following page.

More recently, Willstätter (1921) has synthesised tropinone by a method more convenient than that which he employed earlier. Confirmation of the view that tropine and ψ-tropine are inter-

nally compensated results from Barrowcliff and Tutin's (1909) inability to resolve either compound into optically active components, although they were able to effect the resolution of atropine by means of *d*-camphorsulphonic acid.



Tropinone.

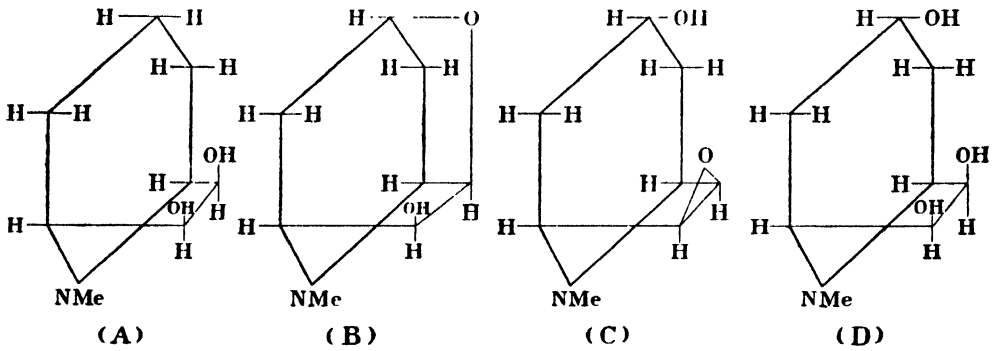
The acid obtained by hydrolysing atropine, *dl*-tropic acid, was first synthesised by Ladenburg and Hundt (1889) by a method unsuitable for the preparation of the acid in quantity. Later, Müller (1918) showed that it could be obtained readily by reducing ethyl formylphenylacetate. This method was also discovered independently by McKenzie and Wood (1919), who, however, preferred another original method, namely, dehydration of atrolactic acid, addition of hydrogen chloride to the atropic acid so formed, and mild hydrolysis of the product $CPhMe(OH)\cdot COOH \rightarrow CPh(:CH_2)\cdot COOH \rightarrow CHPh(\cdot CH_2Cl)\cdot COOH \rightarrow CHPh(\cdot CH_2\cdot OH)\cdot COOH$. The resolution of tropic acid into its optically active components, originally effected by Ladenburg and Hundt, has been studied further by King (1919) and McKenzie and Wood, who have effected improvements in the method. A lower homologue of hyoscyamine, *nor*-hyoscyamine, was isolated from various solanaceous plants by Carr and Reynolds in 1912, and found to yield tropic acid and *nor*-tropanol on hydrolysis.

The tropeines are the esters of the basic alcohol tropine, atropine being tropyl-tropeine. It occurred to Ladenburg (1883) to esterify tropine by means of acids other than tropic acid, and to examine the mydriatic properties of the esters, and in this way he discovered the valuable properties of mandelyltropeine (homatropine). More recently, Jowett, Hann, and Pyman (1906–1909) prepared a very large number of tropeines, which were examined physiologically by Dale and Marshall, when the results showed some connection between the chemical constitution of the tropeine and its physiological action.

Hyoscine was discovered by Ladenburg (1880), and is an ester, yielding on hydrolysis *l*-tropic acid and a base, $C_8H_{13}O_2N$, called oscine, which has been the subject of many important researches during the last few years. Oscine contains two oxygen atoms, but only one hydroxyl group, the second oxygen being attached to two carbon atoms, for Schmidt (1902–1916) found that treatment of oscine with hydrogen bromide and subsequent reduction gave dihydro-oscine. This must be a dihydroxy-tropane having the formula A, since it yields 1-methylpiperidine-2 : 6-dicarboxylic acid on oxidation. The formula of oscine is thus to be derived from A by linking one of the oxygen atoms to one of the carbon atoms, the link in oscine taking the place of two atoms of hydrogen in dihydro-oscine. The difficulty has been to decide to which carbon atom this link is attached, and this has been resolved largely by stereochemical considerations. Oscine is optically inactive, but is capable of being resolved into its optically active components (King, 1919), as is also its benzoyl ester (Tutin, 1910). *apo*Hyoscine, however, which is prepared from hyoscine, no longer contains an asymmetric carbon atom in the acyl residue and is incapable of resolution (King, 1919). It yields on reduction a deoxyhyoscine, which differs from the two

racemic deoxytropylosceines (Hess, 1922). These facts led Hess to suggest that whereas oscine contains an asymmetric carbon atom and has the formula (B), first proposed by King, its formation is due to a change of configuration which occurs on hydrolysis and that the basic portion of hyoscine has the formula (C) which does not contain an asymmetric carbon atom. This suggestion has been confirmed by Willstätter and Berner (1923), who have shown that on hydrolysis by lipase hyoscine yields scopine, represented by formula C, which is very readily converted into oscine by either acids or alkalis.

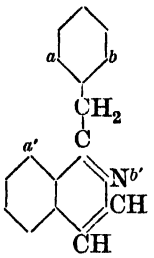
Both formulæ B and C represent anhydrides of trihydroxytropane (D), and King has suggested that D is possibly the formula of teloidine, a substance similar to tropine and oscine, which is obtained together with tiglic acid on hydrolysis of meteloidine. This alkaloid was isolated from *Datura meteloides* by Pyman and Reynolds in 1908.



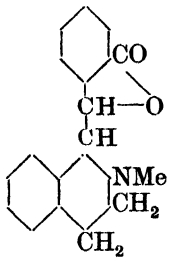
Cocaine was recognised as a derivative of tropane by Willstätter (1898) and its synthesis has been completed by the same chemist and his collaborators this year. The abuse of cocaine has led to the employment in medicine of a number of synthetic local anæsthetics, such as eucaine, stovaine, and novocaine, which are benzoyl esters of basic alcohols in common with cocaine. King (1924) has resolved the two racemic forms of β-eucaine into their optically active components, and has reported on the relative physiological action of the stereoisomerides.

The Quinoline Group.—The alkaloids of this group have not been largely investigated by British chemists. The constitution of quinine and its principal associates in cinchona bark have been established chiefly by the work of Königs and Rabe, whilst King (1922) has contributed to our knowledge of their stereochemical configurations. One of the subsidiary alkaloids of cinchona bark, cupreine, was discovered by Paul and Cownley (1881), whilst others have been characterised by D. Howard (1871–1882) and by B. F. Howard (1905, 1909) and their collaborators. The formulæ of strychnine and brucine, which also belong to this group, are uncertain, but probable formulæ have been deduced by Perkin and Robinson (1910) from the experimental results of Tafel and Leuchs. The investigations of Ewins (1913) have shown that cytisine, the poisonous alkaloid of the common laburnum, also belongs to this group, for he has identified one of the degradation products of this base, obtained by Freund (1901–1906), as 6 : 8-dimethylquinoline.

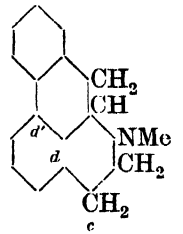
The *iso*quinoline Group.—Most of the alkaloids derived from *iso*quinoline may be referred to one of four main types, which are named and formulated below :



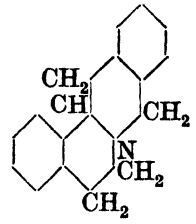
1-Benzyl*iso*quinoline
Type (I.)



1-Meconyl*iso*quinoline
Type (II.)



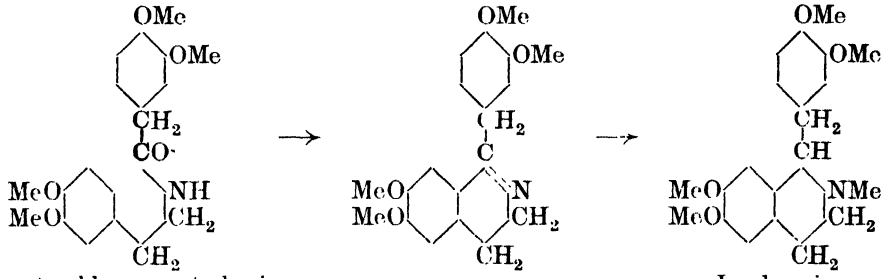
Phenanthreno*iso*quinoline
Type (III.)



Di*iso*quinoline
Type (IV.)

Remarkable progress has been made with this group during the present century, and methods have been evolved for the synthesis of members of each type.

Laudanosine, a derivative of type I, was the first of the opium alkaloids to be prepared synthetically, and was synthesised by Pictet and Finkelstein in 1909 by the dehydration of homoveratroyl-homoveratrylamine, followed by methylation and reduction of the product.



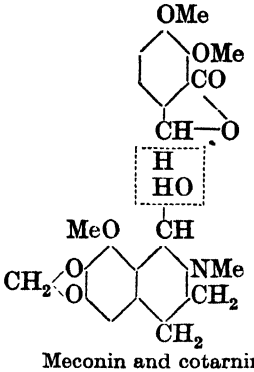
Homoveratroyl-homoveratrylamine. Laudanosine.

Shortly afterwards, Pictet and Gams (1910) synthesised papaverine by a modification of the method, whilst Decker and Kropp effected similar syntheses under different experimental conditions. From compounds of the first type, alkaloids of types III and IV were synthesised later; thus glaucine was prepared by Gadamer (1911) by effecting a junction by means of Pschorr's method between the points *a* and *a'* in a substance of type I, whilst berberine was prepared by Pictet and Gams (1911) by linking together the points *b* and *b'* in a substance of type I through a methylene group.

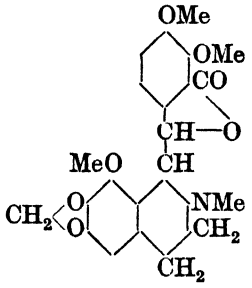
The synthesis of compounds of type I proved also to be important for the synthesis of alkaloids of type II, for Pyman (1909) found that laudanosine and other alkaloids of this type could be oxidised readily to 1-hydroxy-2-alkyltetrahydro*iso*quinolines, thus 1-benzylhydrocotarnine gave cotarnine, and Salway (1910) synthesised 1-benzylhydrocotarnine from myristicin, thus completing the synthesis of cotarnine, which formed the starting point for Perkin and Robinson's synthesis of narcotine (1911), an alkaloid of type II. These authors obtained a small yield of gnoscopine (*dl*-narcotine) by boiling cotarnine and meconin together in alcoholic solution, and resolved it into its optically active components by means of the bromocamphorsulphonates.

Hope, Perkin, and Robinson (1910–1911) found that condensations of this type were greatly facilitated by the presence of nitro- or halogeno-groups, situated in the ortho-position with respect to the methylene group of the meconyl residue, and by making use of such methods

Hope and Robinson (1912) were able to synthesise an optically inactive hydrastine from nitromeconin and hydrastinine. Several methods of preparing the last-named compound, other than by degradation of the expensive natural alkaloid hydrastine, were developed about the year 1913. Decker prepared it by synthetic methods analogous to the synthesis of cotarnine, Freund by the degradation of berberine, and Pyman and Remfry from hydrohydrastinine obtained by the demethoxylation of hydrocotarnine.

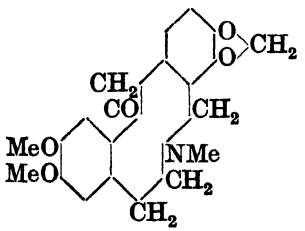


Meconin and cotarnine.

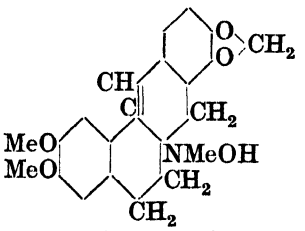


Narcotine.

The constitution of morphine has not yet been completely established. Many formulæ have been proposed for this alkaloid, which when represented by Pschorr's formula appears as a hydro-aromatic derivative of a substance of type III, and certainly some derivatives of morphine, such as apomorphine, belong to this type. The reactions of morphine itself, however, are best explained by a new formula put forward by Gulland and Robinson (1923). This represents the alkaloid as being derived from a phenanthreno*iso*quinoline, in which the carbon atom marked *c* in the formula (III) is linked to both the carbon atoms marked *d* and *d'*, as in pinene. Important work on the constitution of morphine was carried out by Schryver and Lees (1900–1907), who showed that the replacement of the alcoholic group by halogens, and of these again by hydroxyl, gave bases, not identical, but isomeric with morphine. Apart from these investigators, British chemists have taken little part in attempting to determine the constitution of this alkaloid, but Barger (1918) effected the first synthesis of morphol, 3 : 4-dihydroxyphenanthrene, which is a degradation product of morphine.



Cryptopine.



*iso*Cryptopine.

On the other hand, the constitutions and reactions of alkaloids of type IV have been largely elucidated by British workers. Perkin, who earlier (1889–1890) determined the constitution of berberine, has in conjunction with Robinson (1910) slightly modified his formula for this

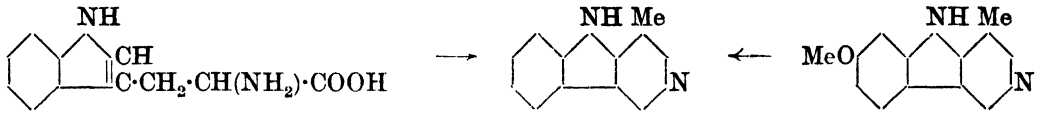
substance, whilst Bland, Perkin, and Robinson (1912) and Pyman (1911–1913) have studied some of the interesting reactions of this base.

In 1916, Perkin determined the constitutions of the rare opium alkaloids, cryptopine and protopine, which contain a ten-membered ring, but are readily converted into substances having formulæ of the di*iso*quinoline type, such as *iso*cryptopine.

He has also studied a number of similarly constituted compounds such as *epi*berberine. The main features of the constitution of corydaline, which is another derivative of a di*iso*quinoline, were determined by Dobbie, Lauder, and Marsden (1897–1902) by a study of the products of its oxidation.

The alkaloids of ipecacuanha also belong to the *iso*quinoline group, for Carr and Pyman (1913–1918) found that emetine yields 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid on oxidation, and have shown the relations between emetine and the subsidiary alkaloids of the root.

The Indole Group.—The chemistry of this group is closely connected with that of tryptophan (α-amino-β-3-indolepropionic acid), one of the amino-acids resulting from the cleavage of proteins, which was first isolated by Hopkins and Cole (1901). Thus, van Romburgh and Barger (1911) found that the base hypaphorine, which occurs in the seeds of a tree grown for its shade in the coffee plantations of Eastern Java, is the trimethylbetaine of tryptophan, from which it may be obtained by methylation and hydrolysis. Furthermore, the base obtained by Hopkins and Cole (1903) by oxidising tryptophan with ferric chloride was identified by Perkin and Robinson (1919) with the substance harman, which O. Fischer (1901) obtained by eliminating the methoxyl group from the alkaloid harmine,



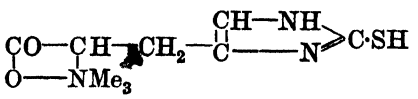
Trytophan. Harman. Harmine.

and as the result of their researches (1912–1919) they proposed for harman and harmine the formulæ shown above.

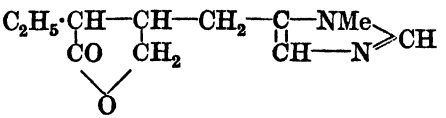
Later, in conjunction with Kermack, Perkin and Robinson (1921–1922) substantiated these formulæ by the syntheses of *nor*harman and *N*-methyltetrahydro*nor*harmine.

It seems very probable that physostigmine, the alkaloid of Calabar beans, belongs to this group. Important work on its constitution has been carried out by Salway (1912) and by Barger and Stedman (1921–1923).

The Glyoxaline Group.—The chemistry of this group also is linked up with that of one of the amino-acids resulting from the hydrolysis of proteins, namely, histidine, which was synthesised by Pyman (1911). Decarboxylation of histidine leads to 4 (or 5)-β-aminoethylglyoxaline, which Barger and Dale (1910) found to be one of the active principles of ergot. In this group again, the trimethylbetaine occurs naturally, for instance in mushrooms (Kutscher), whilst Barger and Ewins (1911) have shown that ergothioneine, a base isolated from ergot by Tanret (1909) is the 2-thiol derivative of trimethylhistidine betaine :



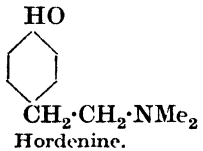
Ergothioneine.



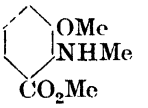
Pilocarpine.

The determination of the constitution of pilocarpine, the principal alkaloid of jaborandi, is almost wholly due to the experimental work of Jowett (1900–1905), for although Pinner and Schwarz (1902) first proposed the formula which is now accepted for this alkaloid, this was based in the first instance on Jowett's determination of the structure of the greater part of the molecule, the homopilopic complex, and confirmed by Jowett's isolation of various derivatives of glyoxaline from the products of distillation of pilocarpine with soda-lime. The point of attachment of the homopilopic complex to the glyoxaline nucleus remained in doubt until the orientation of the dimethylglyoxalines was determined by Pyman (1922), who also isolated, simultaneously with Léger and Roques (1912), a new alkaloid, pilosine, from *Pilocarpus microphyllus*.

The Non-heterocyclic Group.—The isolation and determination of the constitution of hordenine, the alkaloid of barley, are due to Léger (1906), but the substance was first synthesised by Barger (1909) by preparing α-dimethylamino-β-phenylethane, introducing a nitro-group into the para-position, and replacing this by hydroxyl :



Hordenine.



Damascenine.

The constitution of another member of this group, damascenine, the alkaloid of Nigella, was doubtful, until Ewins (1912) reinvestigated the substance and succeeded in synthesising it. In 1909, Barger isolated *p*-hydroxyphenylethylamine from ergot, and developed various syntheses of this and allied bases with his collaborators. The physiological examination of these bases by Dale (1910) enabled the two authors to study the relation between chemical constitution and physiological action in this group.

Alkaloids of Undetermined Constitution.—British chemists have taken an important part in the pioneer work of attacking the problem of the constitutions of numerous alkaloids. In many cases, the investigations have not yet reached the stage where the alkaloids can be assigned to a definite group. It would serve no purpose to give a long list of such substances and their investigators, but attention may be directed to the investigations of the aconitines carried out by *Dunstan* (1894–1905) and his collaborators, the researches of *Barger*, *Carr*, and *Dale* (1907–1918) on the very complicated alkaloids of ergot, ergotinine and ergotoxine, the work of *Ewins*, *Barger*, and Miss *Field* (1914–1923) on yohimbine and the alkaloids of quebracho bark, and the isolation of muscarine by *King* (1922).

THE NITROGENOUS CONSTITUENTS OF THE LIVING CELL

By R. H. A. Plimmer, D.Sc.

Immense progress has been made in the elucidation of the chemistry of the numerous and varied nitrogenous constituents of the animal and vegetable cell during the past twenty years. We have definite information upon the ultimate composition of both animal and plant proteins in terms of their constituent amino-acids. The amino-acids composing the proteins have been found to be the mother substances of those basic compounds, still commonly called the ptomaines, produced during putrefaction and of the alcohols, produced by yeast, forming fusel oil. The composition of the different proteins has led to investigations upon " quality " of protein in nutrition, with the discovery that certain amino-acids are essential for the life and growth of animals. Advance has been made in the synthesis of proteins, the synthetical products being called polypeptides. The specific differences between the blood proteins of various mammals may be due to the arrangement of the amino-acids in the molecule. Polypeptides have been isolated from proteins, and it would appear that the products known as proteoses and peptones are mixtures of polypeptides.

The general structure of nucleic acid, with the stages in its decomposition leading to uric acid formation, has proceeded so far that the final solution may be reached in the near future. The chemistry of the pigments, chlorophyll and hæmoglobin, with their allies and derivatives, is not so obscure, and a distinct advance has been made in the separation of that complicated mixture of fat-like substances grouped as the lecithins or lipins. Whether any of the vitamins belong to the nitrogenous group is as yet unknown.

To nearly all these investigations workers in the British Empire have contributed, and several have been pioneers.

It is interesting to note that there is only one nucleic acid in animal tissues. Nucleic acid is the same substance whether isolated from thymus or liver. Vegetable nucleic acid is again the same in all plants. The basic structure of the lecithins is the same in all organs. Hæmoglobin, in so far as the coloured part of the compound is concerned, is the same in all animals. Proteins are very much the same. Yet each animal and plant is different. Some constituent is evidently placed in a different position, and the general mixture is open to all sorts of variations. In every case, a series of simple compounds is built up into a complex: 18 amino-acids into a protein; 4 basic compounds, phosphoric acid and a hexose (or pentose) into nucleic acid; 4 pyrrole ring compounds into chlorophyll and hæmoglobin. These simpler constituents are not so very complicated. Complication arises from the various combinations and mixtures. Other simple units are still expected to be found helping in this conglomeration.

The Chemistry of the Proteins.—There are so many considerations in the chemistry of the proteins that in order to get a clear view it is preferable to consider them under several headings. A general conception of a protein may be taken to be like a box of mixed biscuits, arranged in rows and layers of various kinds. Each biscuit must then be imagined to be connected to its neighbours, so that if removed they form a continuous chain. Every protein differs as each box contains different biscuits, or the same biscuits are arranged in a different way. A single biscuit represents an amino-acid. A layer of biscuits may be taken to represent a proteose or peptone. If two biscuits were removed the combination would be that of a dipeptide, if three a tripeptide, etc. Those biscuits with sugar on the top may be looked upon as the most important, and many of the others as the filling of the box. It is thus seen that every box has a different value as a food. If the biscuits be taken out and separated, it might happen that a

corner was knocked off from some of them and the broken biscuit might represent a ptomaine; if the top were knocked off we might have an alcohol composing fusel oil. We have to learn the structure of every biscuit, the number and amount of each kind in the box, the order of the arrangement, and other details.

(a) *The Isolation of the Amino-acids.*—It had been known for many years that proteins were resolved on hydrolytic decomposition into a mixture of mono-amino-acids, which were separated from one another by methods based upon fractional crystallisation of the compounds themselves or of their salts. Isolation and characterisation was only effected if one or more were present in comparatively large amount. About 20% was thus identified and the remainder consisted of uncrystallisable syrups.

Drechsel, by the use of phosphotungstic acid, discovered that the mixture contained di-amino-acids as well as mono-amino-acids. Further investigations of these di-amino-acids, or hexone bases, were made by Kossel and his pupils. Their method is the one now used for isolating and estimating this group (1903).

The study of the simple mono-amino-acids by Emil Fischer and his pupils showed that the mixture could be separated by fractional distillation of their esters *in vacuo*. Applying this ester method to casein (1901), and later to other proteins, Fischer was able to advance our knowledge of the mono-amino-acids to 50 and 70 %. He further showed that the amino-acids phenylalanine, serine, and alanine, previously known to be present in only a few proteins, were present in all. Phenylalanine in its distribution was moreover the principal aromatic constituent, for it not only often exceeded in amount that of tyrosine, but occurred when the latter was absent. Two new compounds, proline and hydroxyproline, were found by this method.

The ester method has come into general use in all parts of the world and many improvements have been made in the actual details, the present procedure being mainly elaborated by Levene. Osborne has used it in his extensive and well-known work on the vegetable proteins.

Both the ester method and that of Kossel have been used in many laboratories in the British Empire. Foreman, in Cambridge, has made improvements and thus has obtained larger amounts of certain amino-acids.

The separation of amino-acids from complex mixtures has been effected by Buston and Schryver by an adaptation of the carbamino-method of Siegfried.

Tyrosine and Cystine.—The ester method is not applicable to the isolation of tyrosine and cystine. These two amino-acids are characterised by insolubility in aqueous solution. At present, cystine is the only known sulphur containing amino-acid, so that its amount in a protein may be estimated by a sulphur determination. With few exceptions, it has been isolated only from those proteins (scleroproteins) which contain a considerable quantity. The amount of tyrosine obtained by crystallisation is probably less than is actually present. Folin's colorimetric method indicates larger amounts.

The separation of these two insoluble amino-acids has presented certain difficulties. Plimmer found that their separation could be quantitatively accomplished by an adaptation of the ester method. Tyrosine is easily esterified by alcohol containing hydrochloric acid, and goes into solution, whilst cystine is unchanged and does not dissolve.

Tryptophan.—The amino-acid, tryptophan, discovered by Hopkins and Cole in 1901, needs a special method for its isolation. It is precipitated from a tryptic digest of a protein by mercuric sulphate in acid solution. No other way has yet been found for its isolation, and in consequence of the difficult nature of the process it has not been separated from many proteins. It is not

possible to separate it after acid hydrolysis on account of its total destruction by boiling with acids.

The isolation of tryptophan gave the explanation of three phenomena long known in connection with the chemistry of the proteins, (1) the reddish-violet colour given on adding bromine water to a tryptic digest of a protein, (2) the Adamkiewicz reaction, (3) the origin of indole, scatole, and related substances in putrefaction. Tryptophan gave all these reactions vividly. The Adamkiewicz reaction was also found by Hopkins and Cole to be due to the presence of glyoxylic acid.

Hydroxyglutamic Acid.—Dakin (1918) introduced a new procedure into the usual routine for separating the mono-amino-acids. He found that the simple mono-amino-acids together with proline were dissolved from the mixture in neutral aqueous solution by butyl alcohol. They were thus obtained separate from the di-amino-acids and the dibasic acids, and it was thus easier to isolate them in greater quantities. On examining the dibasic fraction, a new constituent of proteins was obtained. This substance was identified as hydroxyglutamic acid. The process of extraction was improved in 1920 by the erection of an apparatus by which the butyl alcohol could be used as extractive *in vacuo*. Hydroxyglutamic acid has been found in casein, glutelin, gliadin, and zein, but not in gelatin.

Composition of Proteins.—The analytical results obtained by these methods may be illustrated by the table on p. 206. These data are selected as showing the best results that have as yet been obtained and they include the figures of Dakin. In no case do the totals reach 100; the incompleteness is mainly due to the difficulty of separation even after the several fractions have been prepared.

Constitution of the Amino-acids.—In certain cases the exact constitution of an amino-acid has been troublesome to make out, but in all cases it is now definitely known, and further every amino-acid has been prepared by synthesis. It must be noted that except glycine the amino-acids possess asymmetric carbon atoms and can exist in two or more optically active forms. The natural optically active form has also been prepared.

The synthesis of histidine was first effected by Pyman and that of hydroxyglutamic acid by Dakin.

For methods of synthesis the reader is referred to books dealing with the chemistry of proteins.

Abbreviated Methods of Analysis.—Several methods have been described for determining the amount of individual amino-acids. They are mainly in connection with those compounds which give colour reactions, or have other special characteristics.

Colour reactions have been described for tryptophan, histidine, and tyrosine. These methods all suffer from the unstable nature of the colour, or from the colour being developed by more than one amino-acid. The best known of these methods is that for tyrosine; it gives values considerably higher than the figures obtained by isolation.

Attempts have been made to estimate tyrosine by bromination by Brown and Millar and by Plimmer and Eaves. The concurrent reaction of tryptophan and histidine with bromine unfortunately leads to uncertain results. By taking advantage of the different manner of combination of nitrogen in the various amino-acids Van Slyke (1911) brought out a most ingenious method of estimating seven separate groupings. It depends largely upon the estimation of amino-nitrogen by the action of nitrous acid. For this purpose, a special form of apparatus, in both a macro- and a micro-form, was devised. Excellent results were given by most of the amino-acids. Arginine was estimated by decomposition by strong caustic potash, but 20 % alkali

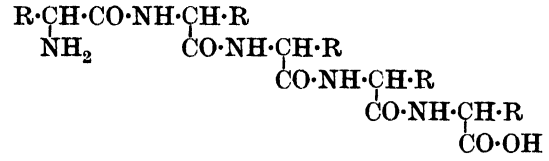
was found sufficient by Plimmer. The action of nitrous acid upon the hexone bases was also studied by Plimmer, and in the case of arginine the amount evolved depended upon the time of the reaction. On the whole, the method gives fairly satisfactory results, but discrepancies

	Gelatin.	Caseinogen.	Zein.	Gliadin of Wheat.	Globin from Hæmoglobin.
Simple mono-amino-acids :					
Glycine	25·5	0	0	0	0
Alanine	8·7	1·5	3·8	2·0	4·2
Valine	0	7·2	0	3·4	
Leucine	7·1	9·4	25·0	6·6	29·0
*iso*Leucine	0		0		
Mono-amino-dibasic acids :					
Aspartic acid	3·4	3·8	1·8	0·6	4·4
Glutamic acid	5·8	21·0	31·3	43·7	1·7
Hydroxy-amino-acids :					
Serine	0·4	0·5	1·0	0·2	0·6
Hydroxyglutamic acid	0	10·5	2·5		
Amino-acids with aromatic nucleus :					
Phenylalanine	1·4	3·2	7·6	2·4	4·2
Tyrosine		4·5	5·2	1·2	1·3
Amino-acid with indole nucleus :					
Tryptophan	0	1·7	0	1·0	
Heterocyclic acids :					
Proline	9·5	8·0	8·9	13·2	2·3
Hydroxyproline	14·1	0·3			1·0
Hexone bases, or diamino-acids :					
Arginine	8·2	3·8	1·6	3·2	5·4
Lysine	5·9	6·0	0	0·2	4·3
Histidine	0·9	2·5	0·8	0·6	11·0
Thio-amino-acid :					
Cystine	0			0·5	0·3
Ammonia	0·4	1·6	3·6	5·2	
Total	91·3	85·5	93·1	84·0	69·7

occur. Analyses of globin by Hunter and Borsook suggest that the globin molecule contains 2 of tryptophan, 4 of tyrosine, 4 of arginine, 8 of histidine, 10 of lysine, and 100 of other amino-acids.

Polypeptides.—The combination of the amino-acids in the protein was also a subject of research by Emil Fischer. Three methods of synthesis were elaborated by him, and it was shown that

the amino-acids were combined in the protein in acid amide form, *i.e.* the amino-group of one amino-acid was combined with the carboxyl group of another. In this way long chains could be built up :—



These combinations were called polypeptides. If two amino-acids were in combination, a dipeptide resulted, if three, a tripeptide, etc. The most complex peptide that was made was an octadecapeptide. Many of these polypeptides gave the biuret reaction, and some of the simpler ones were salted out by ammonium sulphate, properties associated with proteins and their products, the proteoses, and peptones. Further, some of these peptides were hydrolysed by the action of trypsin. It should be noted that if even two amino-acids be combined two isomers are possible, *e.g.* glycyl-tyrosine and tyrosyl-glycine. The isomers become greater in number as the number of amino-acids in the molecule increase. The synthesis of a natural protein thus becomes a matter of chancing upon the correct order of arrangement. Some idea of the order was given by the action of trypsin, *e.g.* glycyl-tyrosine was hydrolysed, but not tyrosyl-glycine. The isolation of some simple peptides also gives a clue to the arrangement.

Specificity of Proteins.—The order of arrangement of the amino-acids is the most probable explanation of the special nature of proteins of the same class, *e.g.* the caseins of various milks, the proteins of different bloods. These proteins are so alike in their general and physical characters that they are usually regarded as the same. The analyses of the amounts of the amino-acids are also very similar. Biological experiments indicate that some real difference exists, largely from the fact that on injection into the blood-stream specific precipitins are formed.

Kossel and Weiss (1909) observed that the optical rotation of a protein changed on keeping it in dilute alkaline solution for several days. No appreciable hydrolysis was thus caused, but if complete hydrolysis were subsequently carried out racemised amino-acids resulted. This change in the rotation of the amino-acids was considered by Dakin (1912) to be due to tautomeric change of the usual keto-form of the acid amide linking to the enol :



In this transformation the unaffected carbon atom stands at the end of a chain. The position of the optically active acid on hydrolysis of protein treated with alkali is thus given.

Applying this method to gelatin, lysine and glutamic acid were isolated in optically active form. Dakin and Dudley similarly treated casein of cows' milk, and Dudley and Woodman compared it with casein from sheep's milk. Optically active tyrosine and lysine were obtained from sheep's casein, but not from cows', optically active proline from both. The two caseins would thus differ in the order of arrangement of the amino-acids.

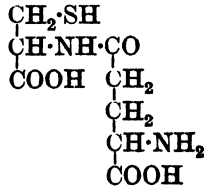
Dudley and Woodman tested the eu- and pseudo-globulin of milk and could find no difference between them. These two proteins commonly found in blood-serum had previously been studied

by Chick and found to be very closely related; the euglobulin appeared to be formed from pseudo-globulin by interaction of this colloid with lipoid. Hartley's careful analysis of these two proteins also indicated their identity. The milk globulins have been found by Crowther and Raistrick to give the same amino-acids as those of blood-serum, from which it is concluded that these globulins diffuse from the blood into the milk. The opposite occurs in the case of the albumins. Lactalbumin differs in composition from serum-albumin and appears to be made in the mammary gland like casein. The crystalline proteins of the albumins of hens' and ducks' eggs are similar in properties and composition. Dakin has examined these two proteins by alkali treatment and subsequent hydrolysis and has found a different arrangement of the constituent amino-acids, and Dale, who tested them as specific antigens in anaphylaxis, has found them different. The order of the arrangement in all probability is the cause of specificity.

Glutathione.—This peptide has much greater significance in biochemistry than its purely chemical structure indicates, for it appears to be intimately concerned in the respiratory processes of the living cell.

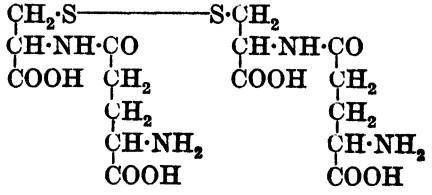
Many years ago de Rey Pailhade observed that extracts of yeast and animal tissues were able to reduce sulphur to hydrogen sulphide, and he claimed that these labile hydrogen atoms had important respiratory functions. The reducing power of tissues was studied by Heffter (1908) and by Arnold (1911) with the use of sodium nitroprusside. Arnold concluded that cysteine was the substance in the cells responsible for the reaction. Heffter, however, first suggested that the presence of labile hydrogen atoms in the SH– group of cysteine might be concerned in the reduction processes and indirectly in the oxidation effects of the cell. For continuous action the spontaneous oxidation of the SH– group to the disulphide –S–S– group must be reversible, and he imagined that the cell possessed some reducing substance (behaving like a sulphite) which would accept the oxygen of a water molecule, leaving the hydrogen to reduce the –S–S– group to SH–. The substance actually responsible for the reaction is the dipeptide, named glutathione, composed of cysteine and glutamic acid isolated by Hopkins (1921) from yeast and other tissues, in which it is present to the extent of 0·01 to 0·02 %. Its exact composition was determined by Quastel, Stewart, and Tunnicliffe (1923) to be that of

glutamyl cysteine :



which on oxidation passes into

diglutamyl cysteine.



The substance is readily oxidised in neutral or faintly alkaline solution, and the oxidised form is easily reduced by zinc and sulphuric acid or by a bisulphite. It oxidises more slowly than cysteine. The existence of the dipeptide rather than cysteine in tissues seems to be due to the resistance of the combination to metabolic changes.

Several theories concerning the mechanism of the oxidation and reduction processes of the living organism have been put forward during the last twenty years. Glutathione in its behaviour agrees with the hydrolytic oxidation–reduction idea of Bach, or the simpler activation of hydrogen supposition of Wieland. According to the former, the reduction of one substance by the H-ion

is associated with a simultaneous oxidation of another by the OH-ion. Wieland's theory of activation of hydrogen modifies Bach's idea; the agent acts as a dehydrase, making hydrogen atoms available for an acceptor. The typical example of combined oxidation and reduction by a tissue is that of milk. Milk will not reduce methylene-blue, or oxidise salicylic aldehyde singly, but if both are present, the one is reduced and the other oxidised. Wieland supposes the aldehyde to exist in its hydrate form; two of its hydrogen atoms are then activated by the tissue and made available for an acceptor. The acceptor may be (1) oxygen, (2) methylene-blue, (3) another molecule of aldehyde. In each case the aldehyde is oxidised to the acid, in case (1) water is formed, in case (2) methylene-blue is reduced, and in case (3) another molecule of aldehyde is reduced to the alcohol —a Cannizzaro reaction.

The dipeptide in its oxidised form can act as H acceptor, and in its reduced form as oxygen acceptor, or hydrogen donator. In the reversible change, it will be observed that only the sulphur atoms are concerned :

$$\text{—SH HS—} \qquad \text{—S —S—} + H_2$$

Hopkins proceeded to show that the cell had the power of reducing the disulphide and oxidising the thiol form. Fresh tissue, even after treatment with alcohol, was found capable of reducing the disulphide, and oxidation of the thiol form occurred on allowing a tissue to autolyse with it under anaërobic and aseptic conditions. The conditions under which the tissue effects the reversible change depend on the reaction of the medium, as is easily seen by examining the reaction with the disulphide in presence of methylene-blue. In slightly acid medium ($p_H = 6{\cdot}8$), both substances compete for hydrogen and little change occurs; in faintly alkaline solution ($p_H = 7{\cdot}4$) the methylene-blue is rapidly reduced, in fact the reaction is actually accelerated in such a way that the dipeptide behaves in the manner of a co-enzyme. Glutathione really acts as an intermediate reducing agent, the oxidised form being again reduced by the tissue. The factor in the tissue is thermostable, but destroyed by oxygen and hydrogen peroxide as shown by Hopkins and Dixon (1922). Other similar sulphides also accelerate the reduction of methylene-blue by the tissues, *i.e.* act as a catalyst. It seems probable that the factor in the tissue is another sulphur-containing substance of this type.

In connection with oxidations by the cell, the observations of Morgan, Stewart, and Hopkins that milk, in presence of methylene-blue as hydrogen acceptor, oxidises hypoxanthin and xanthine to uric acid are of interest. The latter substances act thus as oxygen acceptors.

Insulin.—The preparation of the active substance contained in the internal secretion of the pancreas in a suitable form for medicinal use in combating diabetes was announced in 1922 by Banting and Best, thirty-three years after the connection of the pancreas with this disease had been demonstrated by Minkowski and v. Mering. During the intervening years many attempts to prepare the active substance had been made; some were nearly successful and proved without doubt that the islet cells of the gland produced an internal secretion concerned in the metabolism of glucose. In preparing the active material, Banting and his colleagues prevented the destructive action of the trypsin of the gland by working in acid media, and by using alcohol as solvent avoided contamination with protein. Several other workers were near this discovery, notably Murlin and his various colleagues. These workers have made many important observations upon the preparation of the substance. Certain plant extracts have been found by Collip to possess the property of lowering the amount of sugar in blood; the substance in these extracts has been called glucokinin.

Improved methods of preparation and a careful examination of the properties of insulin were made by Dudley (1923). The purest specimens of insulin gave the biuret, the Pauly and organic sulphur tests for proteins; the glyoxylic acid reaction was not given and Millon's reaction was faint. This specimen was precipitated as picrate and converted into hydrochloride. The potent action of the substance was destroyed by the action of pepsin and trypsin. It was concluded that insulin was a somewhat complex polypeptide; its synthesis is therefore likely to present some difficulty.

The potency of insulin is judged from its power of reducing the amount of glucose in the blood. 0·5 to 1 mgm. of Dudley's pure preparation as hydrochloride reduced the blood-sugar of a 2 kilo. rabbit from 0·1 to 0·04 % and caused hypoglycæmic convulsions.

Putrefaction Bases, Amines.—Concurrently with the evolution of the chemistry of the proteins and amino-acids, the structure and origin of the so-called ptomaines and other basic compounds were studied and made clear.

Amines, corresponding to nearly all the known amino-acids, have been found to occur as products of putrefaction. They are formed by the action of bacteria upon the amino-acids, the general result being expressed by the equation :

$$R{\cdot}CH(NH_2)COOH = R{\cdot}CH_2{\cdot}NH_2 + CO_2,$$

but more probably, since formic acid is also a product, simultaneous reduction takes place as follows :

$$R{\cdot}CH(NH_2)COOH + 2H = R{\cdot}CH_2{\cdot}NH_2 + H{\cdot}COOH.$$

The dibasic amino-acids, aspartic and glutamic, by a similar process give rise to ω-amino-acids :

$$HOOC{\cdot}CH(NH_2){\cdot}CH_2{\cdot}COOH = H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + CO_2.$$

These acids can also be formed from the di-amino-acids and proline.

The two diamines, putrescine and cadaverine, so long known to be present in putrid flesh, were first shown to have their origin in arginine (ornithine) and lysine by Ellinger. It was believed that the toxicity of decomposing meat was largely due to these substances, but careful research has proved that only the amines derived from phenylalanine, tyrosine, tryptophan, and histidine have any marked physiological action. In this connection the names of Dale, Barger, Laidlaw, and Ewins are intimately associated. These amines produce effects similar to those caused by stimulation of the sympathetic nervous system, and have been called sympatho-mimetic. *iso*Butylamine is the lowest in the series of mono-amines with this action; the next members are slightly more active, and on ascending the series the physiological action diminishes. The introduction of the aromatic nucleus increases the action, tyramine being more powerful than phenylamine, and indole–ethylamine still more. The most powerful amine is histamine or ergamine, derived from histidine. Its effects are most remarkable and have proved of great value in physiology. The extraordinary action of extracts of ergot is due to the action of these bases.

The two very interesting compounds, urocanic acid and kynurenic acid, both discovered in dogs' urine, are formed in the animal body from histidine and tryptophan. Urocanic acid is normally present in dogs' urine. The peculiarity of its excretion seems of the same nature as those anomalies called by Garrod " Inborn Errors of Metabolism." The formation of kynurenic acid has presented the first case of the production of the quinoline ring in nature.

Betaines of most of the amino-acids occur in plants, and have evidently some peculiar function. Ergothioneine was shown by Barger and Ewins to be thiolhistidinebetaine. Though it possesses very little physiological action, its importance may be considered afresh in the light of the properties of glutathione.

Of all the basic substances, the valuable properties of adrenaline make this compound stand in a class by itself. Its isolation from the suprarenal gland by Takamine in 1903 was soon followed by its synthesis. The racemic compound was shown by Cushny to be about half as active as the natural *l*-adrenaline.

The properties of choline have been investigated by Ewins, who has made esters with nitric and nitrous acids. These esters closely resemble the natural muscarine in their physiological action. The old idea of muscarine being the aldehyde of choline is thus incorrect. Choline palmitate was made by Fourneau and Page. It is soluble in water and instantly saponified by a trace of alkali.

Creatine and Creatinine.—The presence of creatine in muscle and of creatinine in urine has excited numerous enquiries into their origin and relation in the animal organism. These enquiries have been stimulated by the adaptation to a quantitative method by Folin of the colour reaction of creatinine with picric acid in alkaline solution. This colorimetric method has been used in all parts of the world for testing for both these compounds. The reaction depends upon the reduction of picric acid to picramic acid. Many other compounds, as pointed out by Chaston Chapman, are able to effect this reduction. Often applied to extracts which contain other reducing compounds, some of the results are of small value, and as Folin has pointed out the reaction must be used with caution.

Creatine of muscle is evidently changed into creatinine of urine, but where and how the conversion occurs is still not quite certain. The excretion of creatinine on a diet free from this substance gives a measure of endogenous metabolism, or the daily extent of the life processes of muscle. The most curious phenomenon is that if creatine be consumed in small quantities up to about one gram it does not appear as creatinine or as creatine in urine. It is apparently retained in the body or catabolised in some unknown way. If larger amounts than one gram be eaten, the excess over this figure is excreted as creatinine. Creatine is excreted instead of creatinine during fasting or in absence of carbohydrate food (Cathcart), and creatine is excreted in certain abnormal conditions. The origin of creatine in the body is not known, but it is probably formed from arginine.

Numerous other basic substances have been isolated from muscle extracts in small quantities.

The Lecithins or Lipins.—Besides fats and cholesterol the cells of plants and animals contain complex substances soluble in alcohol, ether, and other fat solvents. Some of them are particularly characteristic of brain- and nervous-tissue.

Various names have been given to the group. The most suitable is that of Lecithins and allied substances or Lipins, adopted by Maclean. Two main classes were distinguished by Thudichum :

(1) The phosphatides, containing fatty acids, nitrogen and phosphorus.
(2) The cerebrosides, containing fatty acids, nitrogen, but not phosphorus.

Investigations upon these substances are complicated by the fact that many of these bodies are inter-soluble, and it has several times happened that mixtures have been regarded as single

substances. The difficulty connected with work on these compounds is also associated with the unsaturated nature of the fatty acid and the fact that impure solvents, particularly ether, produce decomposition. The actual number of lipins for which there is evidence of chemical individuality is small, and they can all be included in Maclean's simple classification :

Phosphatides.

(*a*) Mono-aminomonophosphatides.
N : P = 1 : 1.
(1) Lecithin.
(2) Kephalin.
(*b*) Diaminomonophosphatides.
N : P = 2 : 1.
Sphingomyelin.
(*c*) Mono-aminodiphosphatides.
N : P = 1 : 2.
Cuorin.

Cerebrosides.

(*a*) Phrenosin.
(*b*) Kerasin.

Lecithin.—Lecithin is the best known member of the group, and is a combination of glycerol with 2 molecules of fatty acid, phosphoric acid, and choline. It is generally given the following constitution :

$$\begin{array}{l} CH_2O\cdot OC\cdot R \\ | \\ CHO\cdot OC\cdot R \\ | \\ CH_2O\cdot PO(OH) \\ \qquad\quad | \\ \qquad\quad O\cdot CH_2\cdot CH_2N(CH_3)_3\cdot OH \end{array}$$

since the glycerophosphoric acid, which has been isolated, is optically active. The existence of the isomer, in which the phosphoric acid is attached to the central carbon atom of glycerol, is, according to Tutin and Hann and other workers, probable. The combination of the choline as salt of phosphoric acid, as was originally supposed, is also not yet entirely excluded.

Different lecithins may occur on account of variation of the fatty acid radical in the molecule. One of the fatty acids appears to be palmitic, the other is unsaturated. The constitution has been established by isolation and characterisation of the various components arising on hydrolysis. Lecithin occurs mainly in egg-yolk, heart, various other organs, and in plant-tissues.

Kephalin.—The quantitative study of the isolation of choline from lecithin by Maclean (1908—09) indicated that another base was present in the so-called lecithin. Shortly afterwards, Trier obtained amino-ethyl alcohol from the lecithin of bean meal ; later he obtained it from the lecithin of egg-yolk. Maclean (1915) found it in heart lecithin, and a very careful examination of the fraction revealed no other basic substance. This phosphatide containing amino-ethyl alcohol, in the place of choline, is considered as having the same structure as lecithin, and has been termed Kephalin. It was first distinguished as a separate compound by Thudichum during his examination of brain-tissue.

According to some workers, the presence of glycerophosphoric acid in kephalin requires confirmation, and final proof of the structure is needed.

The separation of lecithin and kephalin is best effected by Maclean's method of treatment

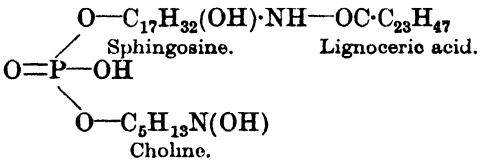
of the cadmium chloride compound of the mixture with ether; the kephalin compound is soluble. Kephalin also differs from lecithin in being insoluble in alcohol.

Cuorin.—This substance, obtained by Erlandsen from heart-muscle, is usually considered as another phosphatide. It is more probable that cuorin is a mixture. The many other phosphatides which have been described are without doubt mixtures.

Sphingomyelin.—Sphingomyelin was found by Thudichum amongst the lipins of brain-tissue; only small quantities are present in other tissues. It has a more complex composition than lecithin or kephalin. Sphingomyelin has been studied by Rosenheim and Tebb, Lapworth, and Levene and West. On hydrolysis, sphingomyelin yields phosphoric acid, 2 molecules of fatty acids and the two bases, choline and sphingosine, $C_{17}H_{35}NO_2$. Sphingosine is given the formula,

$$CH_3(CH_2)_{11}\cdot CH{=}CH\cdot CHOH\cdot CHOH\cdot CH_2\cdot NH_2.$$

Lignoceric acid is one of the fatty acids, the other is probably a hydroxy-acid. Sphingosine is linked in amide form with the lignoceric acid and in ester form with phosphoric acid. Sphingomyelin is given the following formula:



The presence of two fatty acids is explained by supposing that sphingomyelin occurs in two forms, in one of which lignoceric acid is present and in the other the hydroxy-acid. In its constitution it somewhat resembles that of the cerebrosides.

The Cerebrosides.—The cerebrosides are the most characteristic substances which can be extracted from brain-tissue by fat solvents. On account of the fact that the alcohol extract deposits crystals, which on recrystallisation still maintain the same composition, various workers have believed that a special substance, termed protagon, was present in nerve-tissue. Though this idea was abandoned, the claim that protagon was a single substance was revived by Gamgee and Blankenhorn and supported by Cramer. Rosenheim and Tebb's careful study of brain lipins has settled without doubt that protagon is a mixture. These workers have described the most convenient method for extracting the cerebrosides from brain-tissue and for separating them from one another. Many other very important observations were made by them.

The two cerebrosides, phrenosin and kerasin, are very similar in composition. Both yield on hydrolysis galactose and sphingosine; they differ in the nature of the fatty acid, thus

Phrenosin	phrenosinic acid $C_{25}H_{50}O_3$ galactose sphingosine	Kerasin	lignoceric acid $C_{24}H_{48}O_2$ galactose sphingosine.

Rosenheim has suggested that the galactose and sphingosine are combined in glucoside form and that the fatty acid is linked with the sphingosine as acid amide, as in sphingomyelin. This occurrence of two compounds differing in the nature of the fatty acid supports the idea of the existence of two sphingomyelins with different fatty acids.

Rosenheim and Tebb have found that phrenosin in pyridine solution is dextro- and kerasin is lævo-rotatory. The two compounds behave quite differently under the polarising microscope by the so-called selenite plate method. Phrenosin can exist in the form of liquid crystals.

Nucleic Acid.—Miescher discovered nucleic acid in 1874. Kossel (1879—1886) found that thymus nucleic acid gave rise to guanine and adenine on hydrolysis, and Kossel and Neumann (1894) obtained cytosine and thymine together with formic and lævulinic acids. These latter compounds originate from a hexose in the molecule. Yeast nucleic acid (1893) gave guanine and adenine and furfural, with cytosine and uracil. The furfural was produced from a pentose. The composition of these nucleic acids could thus be represented :

Thymus :—	*Yeast* :—
phosphoric acid	phosphoric acid
guanine	guanine
adenine	adenine
cytosine	cytosine
thymine	uracil
hexose	pentose

Since 1903, the constitution of each product has been established except the hexose in thymus nucleic acid. The pentose was identified as *d*-ribose by Levene and Jacobs.

Examination of the nucleic acids prepared from different animal organs by Levene and by Jones and their associates has established the fact that the nucleic acids are identical. Osborne and Harris found wheat nucleic acid to be the same as yeast nucleic acid. The preparation of the vegetable nucleic acid has since been simplified by Clarke and Schryver.

At the same time as these investigations were being carried out, it became clear that the products called nucleoproteins and nucleins were not definite compounds, but consisted of salts of various composition of the polyacid nucleic acid with the polybasic protein. Nuclein is a short term for nucleic acid.

Two other compounds, inosinic acid isolated by Liebig in 1847 from meat extracts and guanylic acid prepared by Hammarsten (1894) from the pancreas, have been thoroughly investigated. They have given the clue to the structure of nucleic acid. Inosinic acid has been shown to be

phosphoric acid—ribose—hypoxanthine

and guanylic acid

phosphoric acid—ribose—guanine.

This type of combination has been called a nucleotide; by careful hydrolysis the phosphoric acid can be eliminated and a compound with pentose and purine base obtained. Inosine was formed from the former, and guanosine from the latter. This type of combination is known as a nucleoside.

The structure of nucleic acid has been found to be that of a tetra-nucleotide consisting of four molecules of mono-nucleotides :

guanine nucleotide	phosphoric acid	—ribose—	guanine
adenine nucleotide	,,	,,	adenine
cytosine nucleotide	,,	,,	cytosine
uracil nucleotide	,,	,,	uracil.

Each of these nucleotides has been prepared and also the corresponding nucleosides.

The tetra-nucleotide structure of nucleic acid is considered by Levene to be that of an ester through the carbohydrate and phosphoric acid :

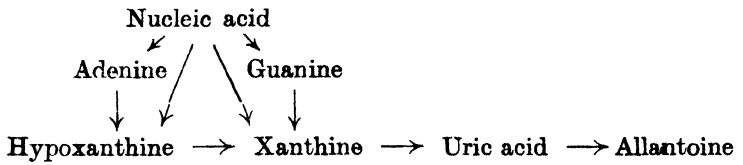
phosphoric acid—pentose—adenine
|
phosphoric acid—pentose—thymine
|
phosphoric acid—pentose—guanine.
|
phosphoric acid—pentose—uracil.

Jones considers the combination is through the carbohydrate nuclei :

phosphoric acid—pentose—uracil
|
phosphoric acid—pentose—adenine
|
phosphoric acid—pentose—cytosine
|
phosphoric acid—pentose—guanine.

It will be noticed that guanylic acid and inosinic acid are mono-nucleotides containing ribose and that animal nucleic acid contains a hexose. No exact explanation of this curious fact has been given, but it seems that the plant nucleic acid enters as food and the mono-nucleotide is retained in the tissues without forming part of the nucleic acid.

Purine metabolism.—The subject of purine metabolism has led to many physiological investigations, largely on account of the importance of uric acid as an excretory product and its relation to diet. Its close chemical connection with the purines has shown that the excretion of uric acid is of two origins, exogenous and endogenous. The former is derived directly from the food, the latter from the daily metabolism of the tissues. The process of breakdown of nucleic acid may be formulated in the scheme :



The purine bases may be first separated and then converted to xanthine, or the conversion may occur before the nucleic acid is hydrolysed.

In man and the higher apes, the uric acid is not oxidised to allantoine, in other mammals the oxidation is more or less complete. In this connection, a large series of animals has been investigated by Hunter and Givens, who term the ratio of the amount of uric acid oxidised to the total the uricolytic index.

The excretion of uric acid or allantoine has been found by Ackroyd and Hopkins in their dietary studies of amino-acids to be dependent on the presence of arginine and histidine. These compounds thus appear to be the mother-substances of the purine ring in the animal organism. Their endogenous origin is thus explained.

BIOCHEMISTRY AND FERMENTATION

By A. HARDEN, F.R.S.

THE present century has witnessed a remarkable development of that branch of chemistry which deals with the changes which occur in living organisms or are brought about by reagents produced by them. The very name Biochemistry, which is now applied to this branch of the subject, is of comparatively recent origin, and its increasing familiarity marks the growing importance of the subject. Stirred to more active life by the classic researches of Pasteur, the study of the chemical relations of living organisms, which had always greatly interested chemists, received further impulses on the one hand from the increasing knowledge of the chemical constitution of the biochemically important substances—the sugars, proteins, and purine derivatives—which resulted from the researches of Emil Fischer, and on the other from the results of the intensive study of Physical Chemistry during the last quarter of the nineteenth century. The combined effect of these various influences was that the investigation of biochemical problems underwent a very noteworthy increase both in Europe and America during the early years of the present century. Almost simultaneously three new journals dealing with the subject—The *Biochemical Journal* in England (1906), the *Journal of Biological Chemistry* in America (1905), and the *Biochemische Zeitschrift* in Germany (1906) were added to the literature. In 1912, the *Biochemical Journal*, founded by the late Benjamin Moore, with the aid of Mr. E. Whitley, to whom Biochemistry in this country is also indebted for his endowment of a Chair at Oxford, was taken over by the newly-constituted Biochemical Society, under the auspices of which it still appears. Another evidence of the awakening interest in this subject was the successful publication by Longmans, Green & Co. of a series of monographs on biochemistry edited by Professors Hopkins and Plimmer and written by investigators actually at work upon the subjects treated. Progress has been rapid and uninterrupted, alike here, in America, and on the Continent. Biochemical Chairs have been founded in many of the Universities, and a large amount of very valuable work has been done.

MICRO-METHODS

A marked feature of this progress has been the introduction of micro-methods both for the determination of physical properties and molecular weights, and for analysis and the estimation of special constituents. All countries have shared in the development of this branch of the subject, which is of fundamental importance for biochemistry, since it enables the biochemist to estimate with accuracy the minute quantities of substances present, for example, in the blood, urine, or other body-fluids, and to analyse or identify those minute amounts of pure substances which are too often all that can be obtained. In this country, we may point to Barger's method for the determination of molecular weights, MacLean's blood-sugar estimation, invaluable in the administration of insulin, and Haldane's gas analysis methods, as examples of what has been done, and great advances have also been made in America, especially in the direction of blood analysis, and in Germany, where the micro-combustion of organic compounds was first worked out.

ENZYME ACTION

The close of the nineteenth century witnessed a discovery of peculiar interest to biochemists, in the preparation by Buchner of an extract from yeast which was capable of fermenting sugar in the complete absence of yeast-cells. This experiment furnished the conclusive proof that the

fermentations produced by micro-organisms, in which complex changes are produced involving the rupture of the carbon chain, are essentially of the same order as the simpler hydrolytic and oxidative changes which had long been known to be capable of production in the laboratory by the aid of extracts from the organs or tissues of animals and plants. The active agents in these extracts are known as enzymes, and the result of Buchner's work with yeast, which was soon extended to two species of bacteria, was the conclusion that the fermentations produced by micro-organisms are due to enzymes, developed by the organisms, and capable of acting in the characteristic way after the death of the organism or when separated from the cell in which they were formed. The chemical action of micro-organisms thus became a branch of enzyme chemistry. Buchner's results, coupled with the remarkable observations made by Emil Fischer on the specific character of the enzymes concerned in the hydrolysis of glucosides, directed renewed attention to the whole subject, especially in England, and a number of investigators were attracted to the further study of the problems presented by the chemical changes produced under the influence of enzymes.

A result of fundamental importance was early obtained by Croft Hill, who, in 1903, demonstrated experimentally for the first time that enzyme action is reversible, and thus laid bare the secret of the mechanism by which the innumerable complex substances present in the animal and vegetable organism are produced from the simple compounds which are available to them. He found that the same enzyme preparation was able both to convert glucose in solutions of high concentration into a disaccharide, and in solutions of lower concentration to reconvert the disaccharide into glucose, a condition of equilibrium being in each case brought about. The principle established by Croft Hill in this pioneer work has since been repeatedly verified in simpler cases, such as the production of esters of the fatty acids and of glucosides.

The detailed work on enzymes carried out during the present century is too extensive to admit even of enumeration. The nature of enzyme action has always attracted workers in this country from the time of the classic work of O'Sullivan and Tompson on invertase, and this aspect of the subject has been pursued by many workers and formed the subject of the first of the monographs on biochemistry (Bayliss) to which allusion has already been made.

Early in the century, Adrian Brown showed in the case of invertase that under certain conditions of concentration the rate of action was independent of the concentration of the substrate, and ascribed this phenomenon to the formation of a compound between the enzyme and the substrate which existed for a definite time before splitting up into the regenerated enzyme and the products of hydrolysis. The alternative theories of the formation of definite compounds or of adsorption complexes between enzyme and substrate have been hotly debated, one of the chief supporters of the adsorption theory being Sir W. Bayliss. The investigations of the Armstrongs—père et fils—also form an important contribution not only to our knowledge of the distribution and specific properties of plant enzymes, but also to that of the mechanism of enzyme action, and have been continued in the series of researches in which E. F. Armstrong and T. P. Hilditch have shown the strict analogy which exists between the mode of action of inorganic catalysts and the enzymes of animal or vegetable origin.

Another branch of enzyme chemistry, important alike from its theoretical interest and its bearing on industry, which has attracted much attention in this country is the action of enzymes on starch and the cognate problems of the nature of starch, and the mechanism of its formation and translocation in leaves. The work of Horace Brown and his colleagues on this subject falls chiefly within the last decade of the nineteenth century, but in the hands of Baker, Davis, Ling,

and their colleagues has received notable extensions and is gradually leading to a solution of the problem.

Another line of work which has been intensively pursued is the investigation of the group of oxidising and reducing enzymes, to which may be added catalase. In this connection, reference may be made to the work of the Cambridge Biochemical School on the oxydases of plants, initiated by Mrs. Wheldale Onslow and still being actively pursued; to that on the reducing enzymes of yeast and bacteria, by Harden, Zilva, and Norris; to that on the peroxydase of milk by Zilva, and to that on the oxidising enzymes of milk by Morgan, Stewart, and Hopkins, and by Haas and Hill. The study of the mechanism of biochemical oxidation has led to a discovery of fundamental importance at the hands of Prof. F. G. Hopkins at Cambridge, who has isolated from yeast and animal tissues a dipeptide of glutaminic acid and cystine, christened by its discoverer glutathione. This substance, like cystine itself, readily undergoes reduction to a derivative of cysteine, which in its turn is easily oxidised back to the cystine form. In the tissues it exists in an equilibrium between the reduced and oxidised forms, and affords a mechanism capable of taking up or " accepting " either hydrogen or oxygen and thus assisting in processes either of oxidation or reduction. It appears also to have catalytic properties in some reactions and to play an important part in the biochemistry of the cell.

Alcoholic Fermentation

Buchner's discovery, to which allusion has already been made, aroused universal interest among biochemists. Buchner himself with a numerous band of colleagues made a very thorough investigation of the properties and capabilities of yeast-juice and the various active preparations of yeast which were obtained. As the result of this work, he advanced the theory that the decomposition of sugar into alcohol and carbon dioxide proceeded by way of lactic acid. This idea aroused much criticism from Slator and others, and was finally abandoned by its author. Experiments with English top-yeasts made by Harden and Young at the Lister Institute from 1903 onwards revealed the fact that the yeast-juice from these yeasts differed in many minor respects from that from bottom yeasts with which Buchner had worked.

Further investigation showed that yeast-juice could be separated by ultra-filtration into two fractions, neither of which alone would bring about the alcoholic fermentation of sugar, whilst active fermentation ensued when the reunited fractions were employed. To the thermostable filtrate the name of coenzyme or coferment was given, the thermolabile residue being regarded as the enzyme. All attempts to isolate the coenzyme have so far failed, but it has been shown by Neuberg that a mixture of α-ketonic acids is able to produce the same effect as the coenzyme, whilst Harden found that acetaldehyde was also capable of bringing about the same result.

Harden and Young also observed that the addition of phosphates produced a remarkable acceleration in the rate of evolution of carbon dioxide, and that at the same time the phosphate became converted into a form which no longer gave a precipitate with magnesia mixture. A similar observation was made about the same time by Ivanov in Russia. Further examination showed that the reaction in presence of phosphate and sugar could be quantitatively represented by a simple equation, according to which half the sugar was converted into alcohol and carbon dioxide and the other half into a hexosediphosphate, $C_6H_{10}O_4(PO_4Na_2)_2$. This substance was then slowly hydrolysed by a specific enzyme, hexosephosphatase, yielding a hexose and a phosphate, both of which again entered into reaction along with a further quantity of sugar. The hexose-

phosphoric ester was isolated in the form of its salts and has been investigated by many workers, including Young, Lebedev, Euler, and Neuberg. Its exact function in the process of the breaking down of the sugar molecule is still not clear, but the interest attached to it has been greatly increased by the fact that it, or a closely allied compound, has been found by Embden in muscle and is considered by him to form an essential stage in the production of lactic acid from glycogen which accompanies muscular work. It has also been suggested that it, or an analogous compound, occurs in blood, and is also an important factor in the deposition of bone (Robison).

The formation of this compound is not in all cases a simple esterification of the hexose molecule, since the same compound is produced from glucose, mannose, and fructose, and, however prepared, yields fructose on hydrolysis with acids. It seems, therefore, most probable that its production is associated with the early stages of the decomposition of the sugar, and that it is essential for this purpose, since in the absence of phosphate fermentation does not proceed.

More recently a monophosphoric ester has also been isolated from yeast-juice fermentation products (Harden and Robison). It differs in properties from a compound of the same composition obtained by partial hydrolysis of the diphosphate (Neuberg), and its relation to this compound and to the process of alcoholic fermentation has not yet been ascertained.

Many attempts have been made to accelerate the rate of fermentation produced by living yeast, but this is not easily accomplished. Euler in Sweden and Neuberg in Germany have both observed instances of this effect by the use of a great variety of substances, but much greater accelerations can be produced with yeast-juice, dried yeast, etc. An immense number of substances have been examined in this respect by Neuberg, and many found to be active. Among these are many reducible substances. The effect of these was analysed by Harden and Henley, who found that it was largely confined to the reaction taking place in presence of free phosphate and did not affect the normal rate of fermentation, the acceleration ceasing when the free phosphate had been converted into hexosephosphate. In agreement with Neuberg, they ascribe this to the action of the added substance as an acceptor for hydrogen, in presence of which the phosphate reaction can rapidly attain its maximum rate.

Important investigations on the chemical dynamics of fermentation by yeast and on yeast growth have been published by Slator at intervals from 1906. He has been able to establish formulæ connecting rate of growth and rate of fermentation, and has also studied the effect of the products of fermentation on the rate of growth and has made interesting experiments on the vexed question as to the influence of oxygen on the growth of yeast, which had previously been investigated by Adrian Brown, Horace Brown, and others. One of the chief functions of oxygen in this respect is the negative one of removing the carbon dioxide which acts as a strong inhibitor.

Other interesting studies on the chemical action of yeast are those of Mrs. Smedley MacLean and Miss Hoffert on the formation of fat and reserve carbohydrate by yeast. No simple substance could be found which could be regarded as capable of acting as an intermediate product in the formation of these substances from the sugars. The formation of reserve carbohydrate—largely glycogen—is most easily effected from maltose—an interesting result in view of the most recent work of Irvine on the presence of the maltose residue in glycogen. Fat is readily formed from the sugars in presence of oxygen, much less readily in its absence. Phosphate enters the yeast-cell in proportion to the concentration of the sugar solution in which it is dissolved, and has a favourable influence on the production of fat. This affords a striking proof of the great significance of phosphates for the metabolism of the yeast-cell.

Chemical Action of Bacteria

Towards the end of the nineteenth century P. F. Frankland carried out many experiments in which bacteria were the agents of chemical change. These researches, the direct outcome of Pasteur's work, were chiefly directed towards the determination of the nature of the products of bacterial action and the utilisation of their selective action on different stereoisomerides. Work of the former kind was also undertaken about 1900 by Harden, who examined the products of the fermentation of glucose and allied compounds by organisms of the *Bacillus coli* group. These chemical actions had long been qualitatively employed by bacteriologists for the discrimination and identification of various species of bacteria. The results obtained showed a certain degree of regularity, exemplified by the production of acetic acid and alcohol in molecular ratio, and some dependence on chemical structure, mannitol giving about twice as much alcohol as glucose. More recent and more varied experiments on the same subject by Grey have shown, however, that some of these regularities depend on the maintenance of constant conditions of experiments. Grey concludes from his work that comparatively few enzymes are concerned in the breaking down of the various substances susceptible of bacterial decomposition. He also showed that several distinct stages, characterised by entirely different chemical changes, occur in the action of the organism on glucose.

By working in presence of formates, which, as shown by Pakes and Jollyman, are decomposed by *B. coli* into carbonates and hydrogen, he has been able to demonstrate the action of this organism on many hydroxy-acids, etc., which are not attacked under the ordinary conditions of experiment.

Adopting the principle of trying to account for the whole of the fermented sugar, Harden and Walpole found that about one-third of the glucose changed was converted by *B. lactis aerogenes*, an organism at that time not very definitely distinguished from *B. coli*, into 2 : 3-butylene glycol. It was subsequently found (Harden and D. Norris) that this substance could be produced by the organism from acetaldehyde. Grey, moreover, found traces of acetaldehyde among the products of fermentation of glucose by *B. coli*, and suggested that it was an important intermediate product, thus anticipating Neuberg, who later showed its increased production in presence of a " fixation " agent such as sodium sulphite.

Several investigations of the products formed by anaërobic bacteria from glucose, etc., have been carried out by Wolf and his colleagues, and an elaborate study of the metabolism of the Timothy grass bacillus, with special reference to the formation of fat, has been made by Stephenson and Clark at Cambridge.

A very important application of bacterial fermentation was made during the War to the large-scale production of acetone and butyl alcohol from starch. An organism capable of bringing about this reaction was isolated by Fernbach and used for this purpose. In the subsequent development of a practical method for the British Admiralty Weizmann employed a similar organism. It appears to act by producing as intermediate products acetic and butyric acids, from which acetone and butyl alcohol are then formed by secondary reactions. Large volumes of carbon dioxide and hydrogen are given off during the process.

Much work has also been done in a somewhat different direction, the investigation of the action of bacteria on nitrogenous substances. In this connection, the experiments of Barger and his colleagues on the production of physiologically active bases by the bacteria of putrefaction are of great importance. Systematic investigations have also been carried out at Cambridge

by Raistrick and others on the decomposition of nitrogenous substances of known structure by bacteria, which throw much light on the mode of action of these organisms. Among much other work, that of McLeod and Gordon may be noticed. They have demonstrated the production of hydrogen peroxide by pneumococci and many streptococci, the effect being that the development of the organism is rapidly checked by the accumulation of this bactericidal substance.

Vitamins

One of the most notable achievements in biochemistry is the discovery of the existence of vitamins. Experiments on feeding animals on purified diets, carried out by various investigators from 1888 onwards, had shown that continued well-being was impossible on a diet consisting of pure fats, proteins, and carbohydrates, along with the requisite mineral constituents. Stepp, in Germany (1911, 1912), showed that extraction with alcohol rendered a diet of milk and bread incapable of sustaining mice and that the addition of the extracted matter restored its original qualities to the diet. He fully recognised that some " indispensable dietary unit " was concerned, which was removed by the alcohol. The most decisive experiments and the clearest views on the subject are, however, due to Hopkins, whose work, commenced before 1906, was only published in 1912. He clearly showed that animals may receive a diet containing the requisite amount of mineral matter, carbohydrate, fat, and a suitable protein, and of sufficient energy-producing nature and yet be unable to live; and, further, that the addition of a small amount of milk, comprising less than 4% of the total food intake, was sufficient to render such a synthetic diet complete. He fully recognised the meaning of this result, and drew the conclusion that accessory factors must exist, the presence of which is necessary in any diet adequate for the normal development of an animal. The small amount of substance required to supplement the synthetic diet led him to favour the idea that these accessory factors acted rather as stimulants or catalysts than by merely supplying some organic complex which the animal body is unable to manufacture for itself. This view has been abundantly confirmed, inasmuch as it has now been found that daily doses of the order of 1 or 2 milligrams of solid matter, of which 99% at least is known to be itself inactive, have been found sufficient to render certain diets suitable for the growth of rats. It has now been found that at least three, and probably four, of these accessory factors (now termed vitamins *A*, *B*, and *C*, by a slight modification of a proposal made by Funk) are necessary for the normal growth and life of an animal. Their early investigation was carried out chiefly in Great Britain, where liberal aid was afforded by the Medical Research Council, and in America, with invaluable contributions from Norway in respect to scurvy, and the chief results attained may be very briefly summarised as follows :

1. Vitamin *A* is primarily produced in plants by photosynthesis (Drummond and Coward) and thence passes into the animal body, where it is found associated with fat. Its richest source has been found (Drummond and Zilva) to be the liver-oil and roe of the cod and other fish. These obtain it indirectly from the marine diatoms which form the food of innumerable marine animals (Drummond, Zilva).

When the oil is hydrolysed it remains in the unsaponifiable portion (McCollum and Davis; Drummond and Coward; Zucker) and can be separated from the cholesterol which forms a large part of this residue. Nothing further is known as to its chemical nature. It is soluble in fat solvents, not in water. One of its most important properties is that it is rapidly inactivated by

air or oxygen at a high temperature (Hopkins, Drummond). Animals fed on synthetic diets, adequate in all other respects but free from this vitamin, rapidly cease to grow and ultimately die, adults being less sensitive than young, growing animals.

Another very important effect which in certain circumstances follows the absence of animal fats from a diet is the development of rickets, a disease in which imperfect calcification occurs in the bones. This is undoubtedly due to the absence of a vitamin, and in all probability the active agent, the presence of which in a normal diet prevents the occurrence of the disease, is distinct from vitamin *A*, although it is similar to it in many respects and is present along with it in high concentration in cod-liver oil. It has provisionally been termed the antirachitic vitamin. The work of Mellanby, Chick, Korentchevsky, Goldblatt, and Zilva in this country, and of McCollum and his colleagues, Hess and others, in America, is of the greatest importance in this connection, but the question is too complicated to be further discussed here.

2. Vitamin *B* is found in yeast, in seeds, particularly in the embryo, and in green plants. The study of the disease known as beri-beri, common in the East, by Eijkman and Grijns (Dutch investigators working in Java) and later by Braddon, Fraser, and Stanton, in the Malay States, and by Strong and Crowell, in the Philippines, has conclusively demonstrated that it is of dietetic origin and due to the consumption of a diet deficient in a principle which occurs in the embryo and pericarp of cereals. This principle was carefully investigated by Vedder and Chamberlain in the Philippines and by Funk in this country.

Almost contemporaneously it was recognised in America (McCollum and Davis) that in order to render synthetic diets adequate for the nutrition of rats it was necessary to add two distinct accessory factors (vitamins), one soluble in fat, fat-soluble *A*, now termed vitamin *A*, and one soluble in water (water-soluble *B*, now termed vitamin *B*). This latter is now generally regarded as identical with the anti-beri-beri vitamin (Drummond), as its properties and distribution are almost identical. Its distribution has been carefully examined both here (Funk, Cooper, Chick, and Hume) and in America (Osborne, and Mendel, McCollum, Kennedy, Palmer, Steenbock, Dutcher, and others). It is soluble in water or alcohol, and dialyses about as readily as methylene-blue. It is not inactivated by boiling, but is gradually destroyed at higher temperatures. Unlike vitamins *A* and *C*, it is not affected by air or oxygen. Many attempts have been made to isolate the active substances, but hitherto no success has attended these efforts (Funk, Moore, Suzuki, Abderhalden, Seidell), although highly concentrated preparations have been obtained of which 0·5 milligram daily will protect a pigeon from avian polyneuritis (Seidell). The physiological effects of the deficiency, in addition to the production of beri-beri, have been examined by McCarrison and Findlay in this country, and by Mendel, Cowgill, and Karr in America, as well as by a number of other workers.

3. Vitamin *C*, or the antiscorbutic vitamin. Scurvy has long been recognised as due to a dietetic defect, but the nature of this defect was first accurately investigated by Holst and Frölich (in Norway), who found that guinea pigs were susceptible to the disease, so that properly controlled experiments on the subject could be made with them. They found that the disease was due to the absence from the diet of a principle, soon classed with vitamins *A* and *B* as vitamin *C*, which occurs in green vegetables and fruits and is formed (Fürst) when seeds germinate. Following their methods, elaborate investigations have been made in this country on the quantitative distribution of the vitamin in foodstuffs (Chick and colleagues) and on its properties (Harden and Zilva). The question has also attracted much attention in America (Hess, Givens, McClugage Sherman, and others). Its richest sources are found to be green cabbage leaves, citrus fruits

such as the orange, lemon, and grape-fruit, and the tomato, and it is also present in very varying amounts in other green vegetables, fruits, tubers, and roots.

The effect of heat on this vitamin, of great importance with respect to its inactivation in cooked foods, is complicated by the fact (Zilva) that, like vitamin *A*, it is very sensitive to the presence of oxygen, which rapidly inactivates it at the boiling point, especially in an alkaline medium, more slowly at lower temperatures.

Cabbage cannot be cooked or dried without losing a large proportion of the vitamin (Chick, Delf), whereas fruit juices can readily be evaporated *in vacuo* or even boiled without much loss of potency (Harden, Robison, Zilva, Givens, McClugage), and can be preserved for long periods in acid solutions in absence of air (Zilva). The vitamin is soluble in water or alcohol and dialyses in the same manner as vitamin *B* (Zilva, Miura). Like the other vitamins, it has not been isolated. Starting with lemon-juice freed from citric acid (Harden and Zilva), Zilva, by the elimination of the residual sugar, etc., has obtained a very concentrated preparation, of which as little as 1 milligram (of solid matter) is a daily protective dose for a guinea pig.

The whole subject of vitamins is of the utmost practical importance, as the discovery of these principles has for the first time rendered possible a rational system of dietetics.

CHEMISTRY IN AGRICULTURE.

FOREWORD

By Sir John Russell, D.Sc., F.R.S.

Agricultural chemistry began its career in the early days of the last century under particularly auspicious conditions. The workers engaged on the subject were singularly fortunate in that they found themselves confronted with a problem which had baffled generations of practical men, and which by a series of simple and convincing experiments they were able to solve completely. The problem was to feed the farm crops and so obtain greater growth. Farmers knew that farmyard manure, woollen rags, bones, and salt were effective in a general way, but the quantities available were insufficient, and in the case of rags, bones, and salt there were inexplicable uncertainties and inequalities of action which much reduced their practical value. Chemists set themselves to find out what are the actual plant foods and in what form these can most economically be presented to the crop.

The great names associated with the problem were those of Jean Baptiste Boussingault, who from 1834 onwards carried out a series of brilliant researches on his farm at Bechelbronn in Alsace; Justus von Liebig, whose critical acumen and powers of perception proved most useful in stimulating inquiry and careful thought; and Lawes and Gilbert, who came a little later—beginning in 1843—but carried the researches on to a satisfactory practical conclusion which enabled them to found the great artificial fertiliser industry and incidentally to endow in perpetuity the Rothamsted Experimental Station.

The result of all this work was to show that plants assimilate from the soil nitrates, phosphates, and potassium compounds, and if these are supplied in the form of soluble compounds the plant will make additional growth roughly corresponding in the case of the nitrate with the amounts added. Very large supplies of sodium nitrate, ammonium sulphate, calcium phosphate (which was treated with sulphuric acid to convert it into the soluble "superphosphate"), potassium sulphate, and potassium chloride were found and made available to farmers in the form of artificial manures. After a short period of hesitancy the more progressive farmers adopted these manures. The success was so striking that the farmers of England subscribed in 1850 enough money to build the Rothamsted laboratory and to make it one of the great laboratories of the time—the first and for long the only support given by the farming community in this country to experimental science.

The second period in the development of agricultural chemistry began about 1900, when a new generation of workers came in, who, unfortunately for themselves, had not known the great leaders of the earlier period. They set out with a different purpose; unlike their predecessors, they had no definite practical problem before them; instead they set out to study the soil and the crop, and by their patient labours they have revealed much that was unknown before. They have been able to explain many of the discrepancies between expectation and result which had arisen in the course of fertilising practice, and they gave such precision to the subject that farmers were able to reduce unnecessary expenditure and to obtain better results from their operations than before. And so, although in this modern period agricultural chemists have produced nothing so spectacular as the striking success with artificial fertilisers, they have nevertheless rendered valuable help in a great number of ways to the farming industry at a time when help was much needed, and it can safely be said that science now stands in higher repute with farmers than ever before.

The great advantage of the modern method of studying agricultural chemistry as a subject,

rather than as a series of practical problems, is that a logical development has been attained such as would otherwise be impossible. Investigations are pursued because they add to our knowledge of how plants grow or what is happening in the soil, and not necessarily to solve any particular practical problem. This new knowledge is being made as precise and trustworthy as possible; it constitutes a great storehouse on which inventors can draw, and so opens up the possibility of devising new methods of crop production which may surpass the old as the steam and internal-combustion engines have surpassed the horse. Neither of these inventions was possible until great stores of apparently useless knowledge had been gained. In the following pages several cases are shown, including synthetic farmyard manure and partial sterilisation of the soil, where the new knowledge is already emerging from the laboratory into the realm of practice. Other instances are found in the feeding of animals; recent investigations on vitamins are simplifying and improving century-old practices, while in the realm of dairy work modern knowledge of bacteria is giving a precision and certainty which have raised the making of butter and cheese from a mystery to an exact science. Never have the possibilities of applying science to agriculture been greater, and never, it might be added, have there been happier relationships between the scientific workers and the practical farmers.

One further aspect of modern agricultural chemistry deserves mention. Its logical and systematic development has facilitated the drawing up of coherent courses of instruction for those who live in the country. The teaching can now be made really interesting and inspiring because it is founded on definitely ascertained facts and principles elucidated in the laboratory and experimental fields of the scientific worker.

E. J. R.

THE CHEMISTRY OF THE SOIL AND OF CROP PRODUCTION

By H. J. Page, M.Sc.

At the commencement of the twentieth century the position of agricultural chemistry in this country, as far as crop production is concerned, was briefly as follows. The pioneering work of Lawes and Gilbert at Rothamsted, and of Boussingault and Liebig in France and Germany respectively, had borne fruit in the widespread acknowledgment by the farming community of the value of artificial or " chemical " manures. Ammonium sulphate and sodium nitrate were in common use as nitrogenous fertilisers, while superphosphate and bone manures were the chief phosphatic manures, basic slag being used to a much smaller, though appreciable, extent; potash salts from Stassfurt were being increasingly employed.

Moreover, the specific effects of the different types of fertilisers were tolerably well understood. It was recognised that nitrogenous manuring, besides being necessary on all ordinary soils for the production of a large yield of any crop, was specially beneficial to foliage crops, on account of its effect in stimulating vegetative growth. Phosphatic manures were known to be specially conducive to root formation and to ripening and maturation, so that they were most needed by root crops such as turnips and swedes, and by seed crops, notably cereals in late districts. Potash manures had been shown to be particularly effective in aiding the production of carbohydrates in plants, so that they were peculiarly beneficial to such crops as potatoes and mangolds, which contain a high proportion of starch or sugar.

Lawes and Gilbert's conclusion, from the famous Rothamsted experiments, that the fertilising value of dung was due to its content of nitrogen, phosphates, and alkali salts, and that it could be effectively replaced by a suitable mixture of artificial manures containing these ingredients, had found general acceptance among agricultural men of science, although the farmer still declared that dung was superior to artificial manures.

On the whole, up to 1900 the attention of agricultural chemists had been mainly directed to the study of the directly nutritional aspects of plant growth and crop production, to the relative neglect of the many other factors that also exert a powerful influence on the growth of the plant. The work of agricultural chemists during the past quarter of a century has been largely concerned with the study of these other factors.

Before considering this work in more detail, it is instructive to consider the question, referred to above, of the relative manurial value of dung and artificial manures. Lawes and Gilbert's conclusion that a suitable mixture of artificial manures was as effective as dung appears to be perfectly well founded if we consider merely the yield of crops produced by these two treatments, either for 1843, the first year of the famous Broadbalk experiment at Rothamsted, or the average for a relatively short period of years, as did Lawes and Gilbert, or even the average for the 71 years from 1852 down to the present time.*

TABLE I.

Yields of wheat on Broadbalk Wheat Field, Rothamsted.

Treatment.	Bushels of grain per acre.		Cwt. of straw per acre.	
	1843.	Average, 71 years, 1852–1922.	1843.	Average, 71 years, 1852–1922.
Farmyard manure	22	34·3	13	34·6
Mineral manures + ammonium salts . .	26¼	35·1	15¾	40·2

However, the continued repetition of the experiment on the same plots year after year for so many years has resulted in the accumulation of a large mass of data the detailed examination of which brings out a definite difference between the action of dung and of artificials. A mere inspection of the fluctuation in yields from year to year shows that the crop obtained from the plot receiving farmyard manure is a more steady one than that from the plot receiving only artificial manures; it fluctuates less about the mean. When modern statistical methods are used, the difference is shown still more strikingly. Mr. R. A. Fisher has made a statistical examination of these data and has analysed the relative effects of the various factors operative in causing variation in the yield from the different plots.

It will be seen that not only is the annual variation due to weather less on the plot receiving

* Although the experiments were started in 1843, the scheme of plots was modified in 1852, so that comparable averages for all the plots are only available for the period after that year.

farmyard manure than on that receiving artificials—so that although in good seasons farmyard manure may not give quite such a large crop as artificials, in bad seasons it will not give such a reduced yield as the latter—but also, although the plot treated with farmyard manure shows no signs of soil deterioration after 80 years of continuous cropping with wheat, all the plots manured with artificial fertilisers show a definite deterioration.

Farmyard manure is also found to give better results than artificial fertilisers with root crops and with clover.

It is thus clear that there are factors other than the supply of nitrogen, phosphates, and alkali salts which are operative in causing the superior value of farmyard manure. The other

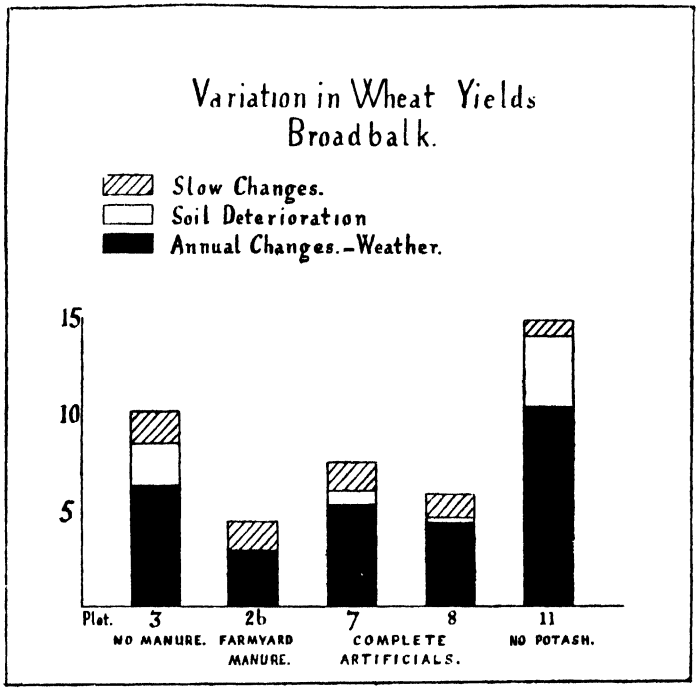


FIG. 1.—Columns showing the amount of variation to which certain Broadbalk plots are liable, with an analysis of the relative effects of the various factors involved (R. A. Fisher).

factors which may affect the growth of plants, and among which the reasons for this difference must be sought, may be classified thus :

(1) The effect of small quantities of elements not formerly supposed to be necessary to plants.
(2) The effect of the physical condition of the soil.
(3) The effect of the reaction of the soil.
(4) The effect of the biological activities in the soil.
(5) The effect of plant diseases.

We are here leaving out of account such factors as illumination, temperature, and the like,

which, although of paramount importance for plant growth, do not call for detailed consideration in the present article.

In recent years, very striking results have been obtained in the study of the effect on plant growth of small quantities of elements other than those known to be essential. Bertrand and Mazé, in France, have studied this subject extensively, and they conclude that in small doses manganese, zinc, fluorine, and iodine produce definite increase in growth in water cultures; in this country, similar results have been obtained with manganese by Dr. Brenchley in water cultures; but in field trials the results were negative, probably owing to the presence of sufficient manganese in the soil already. Silicates also appear to have a beneficial effect. This is especially noticeable on the phosphate-starved plots at Rothamsted; Hall and Morrison conclude that silicates act by causing an increased assimilation of phosphoric acid by the plant. The view has also been advanced, however, that silicates are able to replace phosphates to a certain extent in the plant. This problem is now under investigation at Rothamsted. Voelcker has carried out a long series of pot experiments at Woburn on a variety of inorganic substances. These were all toxic above a certain concentration, but in some cases there was evidence of a stimulating effect when the concentration is low. This appears to be the case with salts of lithium and with borates. The study of the action of the latter has recently been again taken up at Rothamsted, with very striking results. It has been found that in water or sand culture certain leguminous plants, such as the broad bean, are quite unable to make satisfactory growth or to flower and set seed if they are entirely deprived of boron. The most minute trace of boric acid (1 part in 2½ million parts, or even less) suffices, however, to bring about normal healthy growth; moreover, a plant which is almost *in extremis* from lack of boron can be cured and started into healthy growth by the addition of a quantity of boron of the above order. Similar results have been obtained with other leguminous plants such as runner beans and red clover, but in the case of a cereal crop such as barley the effect is not produced. It is at present impossible to say what part these minute traces of boron play in the growth of the plant, nor is there any evidence that plants grown in the field ever suffer from lack of boron, which is present in traces in most soils. Results of this sort do, however, suggest the possibility that the deterioration of soil continually receiving only artificial fertilisers may be due to the gradual removal from the soil of some element which is beneficial to the crop in minimal amounts, and which is present in dung.

The next factor that calls for consideration is the physical condition of the soil. In this connection, there is no question whatever as to the difference in the mode of action of artificial manures and of dung. The dark-coloured, colloidal, humic matter which is present in dung after rotting, or which is produced in the soil from fresh dung and from vegetable residues, exerts a marked effect on the physical condition of the soil, or the soil "tilth." This is reflected, not only in a great improvement in the case of cultivation and in the soil texture, but also in the moisture relationships of the soil; a light sandy soil is given greater body and rendered more drought-resistant, whilst a heavy clay soil is made less sticky and less liable to be water-logged. This effect of the soil organic matter is well illustrated by a comparison of the moisture relationships of adjacent plots on Barnfield at Rothamsted, which receive respectively farmyard manure and no manure. It is found that the moisture content of the soil of the dunged plot is consistently several per cent. higher than that on the adjacent plot which receives no dung. Similarly, on Broadbalk field, the plots of which are underlaid by drains, it is found that drainage water runs from under the dunged plot far less frequently than it does from under those plots

not receiving dung, owing to more water being retained near the surface by the dunged soil. The effect of dung on the mechanical properties of the soil is dealt with below (p. 230).

The mode of formation and the nature of the humic matter of mineral soils are problems which are at present very little understood; the subject is under investigation at the present time. The humic acid which forms a considerable proportion of this humic matter appears to be a true polybasic acid of high molecular weight, the salts of which are of the nature of colloidal electrolytes. Humic acid and the other related constituents of humic matter are derived from vegetable materials, but whether from cellulose or other hexosans, from pentosans or from lignin, is at present uncertain. There is some evidence that they contain furan or phenolic nuclei, or possibly both. Whatever the constitution of the humic matter of the soil may be, the physical properties of this material are of the greatest importance in the present connection. Humic matter is essentially an organic colloid, and it is accompanied in mineral soils by a varying

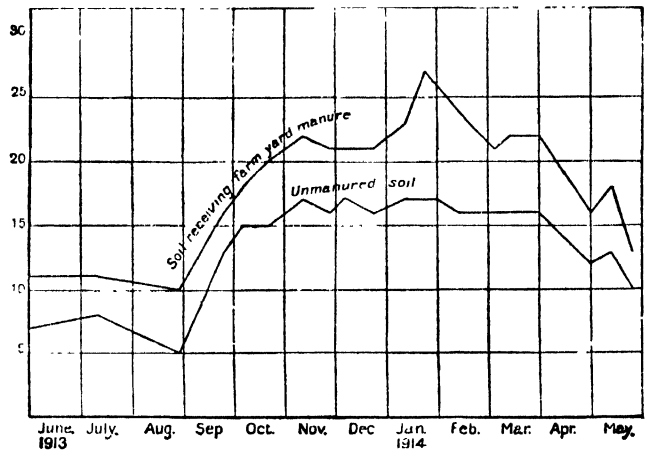


FIG. 2.—Graphs showing the effect of farmyard manure on water content of soils (Broadbalk field, Rothamsted).

proportion of the inorganic colloid known to soil chemists as "clay." * Prior to the enormous development which has taken place in our knowledge of the nature and properties of colloids in the past quarter of a century, the physical properties of the soil were usually thought of as those of a conglomeration of mineral fragments, akin to an artificial mixture of sand grains of varying size. This view was, however, soon found to be inadequate, as it failed to explain many physical characteristics of the soil. Van Bemmelen demonstrated the close similarity between the absorptive power of colloids and the well-known absorptive power of soil, by virtue of which the ammonia and potash of artificial manures are held in the soil and prevented from being lost in the drainage water. Subsequently, more and more attention has been devoted to the colloidal matter of the soil by soil investigators in this country, in the United States, and on the Continent. Several different lines of enquiry have brought converging evidence to bear on the part played by colloids in the constitution of the soil and in its physical and physico-chemical properties. Special mention may be made of the work of Hall and Gimingham, and

* This word is used by soil investigators in a somewhat different sense from that in which it is used in ceramics. It refers to all the mineral particles of soil the diameter of which is less than 0·002 mm.

of Russell and Prescott, on absorption phenomena; of Hall and Morison, and later of Comber, on flocculation; and of Keen, and, later, Fisher, on evaporation. The view which is now becoming well established among soil investigators regards the soil as consisting of a framework of mineral particles which are covered with a colloidal gel coating composed in part of inorganic colloids containing alumina, ferric hydroxide, and silica (probably largely in the form of a colloidal alumino-silicic acid) and in part of organic colloids, the humic materials. The characteristic physical properties of the soil in regard to flocculation, evaporation of moisture, percolation, and so on, admit of reasonable interpretation on this hypothesis, although, of course, the whole subject is still advancing rapidly and much work still remains to be done. The soil moisture, or "soil solution," as it is commonly termed, is regarded as being held in the soil partly in association with this gel coating of the soil particles, and partly, when the moisture content exceeds a certain value, as a free water film.

The composition and concentration of the soil solution are controlled by the absorptive power of the gel coating, which thus has an important influence on the supply of nutrient materials to the plant root. The view, arising largely from van Bemmelen's work, that the absorptive power of the soil colloids was of the nature of a purely physical "adsorption," is now tending to be replaced by one in which the phenomena of soil acidity, basic exchange, and absorption (all of which can be interpreted in terms of the affinity of the soil colloids for kations), may be regarded as the outcome of the existence of acidic groupings in the colloid. It is possible from this point of view to interpret most of the above phenomena on the basis of chemical reactions under stoicheiometrical relationships and subject to the laws of mass action, due regard being paid to the implications of the fact that one of the reactive ions forms part of a colloidal phase. There is, in fact, in modern views a swinging back towards the ideas of the presence in soils of reactive silicates, as originally advanced by Way, with the important difference that the colloidal nature of these silicates is also taken into account.

Before leaving the consideration of the physical properties of the soil, mention may be made of the striking results that have recently been obtained at Rothamsted in the study of the effect of farmyard manure and of chalk on the mechanical properties of the soil. Practical men have long known that both these materials exerted a beneficial effect on the tilth and ease of cultivation of heavy soils. Quantitative expression is given to this fact by measurements which have been made, by means of the dynamometer, of the power consumption in ploughing land which has been dunged or chalked. It has been found that if the draw-bar pull exerted in ploughing unmanured land on the Rothamsted farm be represented by 100, that exerted in ploughing dunged land was 78–82, while for chalked land the figure was 85. This represents an appreciable saving in power, and in cost of cultivation.

The reaction of the soil is another factor of great importance in crop production. The phenomenon of soil sourness is one that is easily recognisable in agricultural practice, being characterised by well-defined symptoms, such as the prevalence of certain characteristic weeds, the liability of cruciferous crops to club root or "finger and toe" disease, and the failure of clover and other leguminous crops. A very large amount of work has been done in recent years on the subject of soil acidity, and considerable confusion of ideas has arisen, although the complexity of the problem is now beginning to be better realised, and the inter-relation of the several factors involved more fully appreciated. In particular, a clear distinction must be drawn between the actual hydrogen-ion concentration of the soil and its titratable acidity. The former value, which may be measured by electrometric, or in some cases by indicator,

methods, is a measure only of the intensity factor of soil acidity. This value does not necessarily bear a direct relation to the amount of base required to bring the soil to neutrality, since this latter depends on the strength of the acid in the soil and its degree of buffering. The many methods of measuring the so-called "lime requirement" of the soil, among which that of Hutchinson and McLennan is one of the best known, give results which thus do not necessarily bear any direct relation to the hydrogen-ion concentration of the soil, but they do give a fair indication of the amount of lime needed to bring the soil to neutrality. They err if anything on the side of giving high results, but that is a good fault from the practical point of view.

The agents responsible for the development of acidity in soils have been the subject of considerable controversy. Following on the older ideas of the presence of special acids such as humic acids, which were supposed to be responsible, it was only natural that with the development of knowledge as to the nature and properties of colloids, a purely physical hypothesis should be advanced, according to which soil acidity was brought about by the selective absorption of the kation of a neutral salt, leaving the anion unabsorbed. This view has now been considerably modified, and the development of acidity in the soil solution is coming to be regarded rather as a function of the state of saturation with bases of the complex acidic colloidal bodies (organic and inorganic) constituting the gel coating of the soil particles. In the same way that a soil well supplied with bases, when treated with a neutral salt, can undergo basic exchange through the replacement of some of the absorbed basic kations by a chemically equivalent amount of those of the neutral salt, in a soil deficient in bases the exchange is one in which hydrogen-ions are liberated and the kations of the salt absorbed. The position is complicated by the fact that acid soils contain soluble compounds of iron and aluminium, which may have been liberated either by direct exchange or by the action of the liberated acid on the insoluble iron and aluminium compounds in the soil. The presence of soluble iron salts in sour soils forms the basis of a valuable test devised by Comber, in which the development of a red colour when the soil is treated with an alcoholic solution of potassium thiocyanate is used as a means of detecting acidity in soils.

Certain indirect effects of fertilisers on the reaction of the soil call for special mention. The two staple nitrogenous fertilisers, ammonium sulphate and sodium nitrate, affect the soil reaction in opposite directions. Ammonium sulphate is a "physiologically acid" fertiliser, while sodium nitrate is "physiologically alkaline." This arises from the fact that the nitrogen in these two substances occurs in the one case in the kation and in the other in the anion. Thus when this nitrogen is absorbed by the growing plant, there remains behind in the soil either sulphuric acid or sodium carbonate (produced by the action of carbon dioxide on sodium hydroxide); hence the long-continued use of these fertilisers tends to produce conditions of extreme acidity or alkalinity in the soil. This is illustrated by some of the experimental plots at Woburn and Rothamsted. At the former, the continued use of ammonium sulphate has brought about conditions of such extreme acidity ($p_H = 4{\cdot}38$) that the barley crop is entirely unable to grow, while on the grass plots at Rothamsted similar treatment has caused the suppression of all except a few acid-tolerant plants which are able to exist under such acid conditions ($p_H = 3{\cdot}79$). The effect of the alkaline residue left by sodium nitrate is most manifest in the sticky, unworkable condition which arises on heavy land after the continued use of this fertiliser, this condition being a consequence of the deflocculating effect which sodium carbonate has on the soil colloids.

The relation of soil acidity to plant growth is still somewhat obscure. Most plants have

acid sap (p_H 4·0–6·8) and make their best growth in media which are slightly acid. Thus an acid soil, in the chemical sense, is not necessarily one that would behave as a "sour" soil from the farmer's point of view. There is now a considerable body of opinion in favour of the view that the harmful effect of sour soils is probably mainly due to the toxic effect of the soluble iron and aluminium compounds in them rather than to their actual acidity. This, of course, does not necessarily apply to extreme cases such as the very high acidity induced by the continued use of ammonium sulphate.

Whatever may be the toxic agent in sour soils, the important practical fact is that the condition is immediately remedied by the application of dressings of lime or chalk in sufficient amount to bring about neutrality. On light sandy soils the value of lime is mainly confined to this effect, while on heavy soils it has the additional *rôle* of flocculating the soil colloids and bringing about a good tilth.

We have so far considered the constitution of the soil and the processes occurring in it wholly from purely physical and chemical standpoints, without reference to the nature of the agents responsible for the chemical changes that occur. By the beginning of the present century it had been definitely shown that certain of the changes in the nitrogen compounds of the soil, collectively known as the "nitrogen cycle," owed their origin to the action of micro-organisms. These discoveries were a direct outcome of the work of Pasteur, and, like the work of that great master, the pioneering work on the biological processes of nitrification and nitrogen fixation was carried out in France.

During the present century an ever-increasing amount of attention has been devoted to the micro-organic population of the soil and to its activities. During the first decade the soil bacteria claimed most attention, but in more recent years the other soil micro-organisms have been extensively studied, as discussed later.

We now recognise at least six distinct phases in the nitrogen cycle in the soil. The complex organic nitrogen compounds which find their way into the soil in the form of animal and vegetable residues, and which consist in the first instance mainly of protein, are first broken down into ammonia, the process being known as "ammonification." This is brought about by a large number of organisms: bacteria, actinomycetes and fungi; it is the biological process in the soil which is probably least dependent on soil conditions, as it proceeds in both acid and alkaline media, and under aërobic or anaërobic conditions. It is uncertain which of the many groups of organisms that are able to effect this change are of the greatest importance in the soil.

The conversion of ammonia to nitrates, or "nitrification," on the other hand, is a very specialised process brought about by three specific organisms, *Nitrosomonas* and *Nitrosococcus*, which oxidise ammonia to nitrite, and *Nitrobacter*, which oxidises the nitrite to nitrate. These organisms are autotrophic; they use carbon dioxide as their source of carbon, assimilating it by virtue of the energy they obtain in the oxidation of ammonia and nitrites. They are all very sensitive to the condition of their environment, being unable to function under acid conditions. The mechanism of the ammonia-oxidation process is at present almost entirely unknown.

The two down-grade processes of ammonification and nitrification are factors of prime importance in the supply of nitrogen to the plant, nitrate being the form in which most plants obtain their nitrogen from the soil. Two other down-grade processes are, however, possible, which, so far from being beneficial, are actually wasteful of nitrogen. One of these is the process of "denitrification," which consists in the reduction of nitrates, often with the evolution of

gaseous nitrogen. Many bacteria can effect this change, but it occurs usually only under anaërobic conditions such as those occurring in water-logged soils, so that the process is not of significance in most British soils, although it is important in tropical swamp soils, as, for instance, in " paddy " fields where rice is grown. There is another process which results in the loss of gaseous nitrogen from soil rich in organic matter under aërobic conditions. The mechanism of the process is at present obscure, but it gives rise to considerable losses of nitrogen from cultivated soils rich in organic matter, such as those which are heavily dunged, or from virgin soils when brought into cultivation. The following table shows the results obtained by the analysis of soil from the dunged plot on Broadbalk field at Rothamsted, and from experiments made by Shutt on freshly broken up prairie soil in Canada.

TABLE II.

Losses of Nitrogen From Cultivated Soils.

	Broadbalk Wheat Field, Rothamsted. 49 years (1865–1914).		Prairie Soil. 22 years (Shutt).
	Rich Soil, Plot 2. lb. per acre.	Poor Soil, Plot 3. lb. per acre.	lb. per acre.
Nitrogen in soil at commencement	0·175% = 4340	0·105% = 2720	0·371% = 6940
Nitrogen added in manure, rain (5 lb. per annum) and seed (2 lb. per annum)	10,140	340	—
Nitrogen expected at end	14,480	3060	6940+
Nitrogen found at end	0·259% = 5950	0·095% = 2590	0·254% = 4750
Loss from soil	8530	470	2190+
Nitrogen accounted for in crops	2500	750	700
Balance, being dead loss	6030	— 280 *	1490+
Annual dead loss	123	— 6 *	68+

The same or a similar process takes place in sewage beds and in manure heaps. The latter case has been recently investigated by Russell and Richards at Rothamsted.

A further loss of nitrogen from the soil occurs by the washing out of nitrates in the drainage water; nitrates, unlike ammonia, are not absorbed by the soil. Only a part of the losses suffered by the Broadbalk soil receiving dung can be accounted for by the nitrate in drainage water, while in the case of the prairie soil there is no percolation.

* Gains.

Against these losses of nitrogen from the soil may be placed the process of nitrogen-fixation, which may be effected either by the nodule bacteria which normally occur in the root nodules of leguminous plants (although they are also capable of independent existence in the soil), or by essentially free living bacteria such as *Azotobacter*, which is aërobic, and *Clostridium*, which is anaërobic. These organisms, by assimilating free nitrogen from the atmosphere and building it up into organic nitrogen in their own cells, help to counteract the losses of nitrogen which have been discussed. Evidence is afforded for the existence of such processes in ordinary soil by the nitrogen balance of the soil of the unmanured plot on Broadbalk field at Rothamsted, shown in Table II. Despite the losses of nitrogen which occur in the drainage water, the sum of the nitrogen removed by the crops during 49 years and the nitrogen now present in the soil is, if anything, greater than that in the soil originally. The nitrogen-fixing organisms are dependent on the reaction of the soil: *Azotobacter* will not act at greater hydrogen-ion concentrations than p_H 6, although the nodule organism is somewhat more tolerant of moderate acidity. Nitrogen fixation is also dependent on a supply of energy material; asymbiotic nitrogen fixation is greatly stimulated by the addition of sugar, straw, or other plant residues to the soil, as shown by Hutchinson and by other workers. The beneficial action that farmyard manure exerts on the clover crop would appear to be similarly a result of the organic products derived from the straw in the manure. It has been shown by Thornton at Rothamsted that the nodule development of leguminous crops is greatly increased by the addition of straw to the soil. In order to get the full effect, however, it is also necessary to add phosphates. These, by provoking greater root development, enable the greatly increased numbers of nodules caused by the straw treatment to develop fully and thus to cause a more vigorous growth of the plant by supplying larger amounts of nitrogen.

The nitrate that is produced in the soil by biological processes may be assimilated, not only by higher plants, but also by soil organisms. So long as these organisms are deriving their energy from the decomposition of organic matter with a relatively high ratio of nitrogen to carbon, this process is not harmful to plant growth, but in other circumstances this competition for nitrate between the growing plant and the soil organisms may be attended by harmful results. This is the case when there is added to the soil organic material free from or relatively poor in nitrogen. In these circumstances the organisms are stimulated to greatly increased growth by the plentiful energy material available, and as there is insufficient nitrogen for their needs in the organic matter, they assimilate the soluble nitrogen in the soil so rapidly that the soil may be almost entirely depleted of nitrogen in a form available to the plant, which thus suffers from nitrogen starvation. Hence the addition of carbohydrate material, although it stimulates nitrogen fixation and thus enriches the soil in total nitrogen, may be temporarily inimical to plant growth. The effect is, however, a transient one; the nitrogen that has been locked up in the cells of the organisms during their rapid growth will later be broken down again as the organisms die and their numbers revert to more normal values, so that treatment with straw or crop residues which would be harmful if applied shortly before the crop was sown may be beneficial if carried out some time beforehand. In these circumstances, also, this temporary locking-up of soluble nitrogen greatly minimises the loss of nitrate that occurs in drainage during the time there is no crop on the land.

Even in the absence of specially added carbohydrate material, it is probable that the assimilation of nitrate by soil organisms plays a large part in the conservation of the soil nitrogen. One of the most surprising facts in connection with the nitrogen economy of the soil is the

great disparity between the total amount of nitrogen in the soil and the amount available for plant growth or for loss by drainage. Even on the unmanured plot on Broadbalk field at Rothamsted, which has been continuously cropped with wheat for 80 years, the total nitrogen content is now a little under 0·1%, corresponding to as much nitrogen per acre, in the top 9 inches of soil, as there is in a dressing of ammonium sulphate of nearly five tons to the acre, a dressing about fifty times as great as that which would, in practice, give a considerable crop increase. Similarly, on the drain gauges at Rothamsted, which are never manured and are kept free from weeds, the loss of nitrogen as nitrates in the drainage water is exceedingly slow. It is thus difficult to avoid the conclusion that the greater part of the nitrogen in the soil is locked up in some form in which it is not available to the plant; part may be tenaciously held in the humic matter of the soil in a form that resists rapid nitrification, but, on the other hand, evidence is accumulating to show that active nitrification is always going on in the soil, and that the accumulation of large amounts of nitrate is prevented by the rapid assimilation by soil organisms of the greater part of that nitrate as soon as it is formed. In other words, the nitrate content of the soil at any moment may be the resultant of two opposing processes, a vigorous nitrification and an almost equally vigorous nitrate assimilation.

The decomposition of non-nitrogenous plant materials in the soil—the celluloses, starches, pentosans, etc.—the products of which we have seen to be of such importance both in their relation to the nitrogen cycle in the soil and as precursors of the humic matter of the soil, is effected by a number of different organisms. The simpler sugars are consumed by the greater number of the soil organisms, but the more complex, insoluble substances, such as cellulose, pentosans, and lignin, are attacked by a more restricted flora. In ordinary soils, the decomposition of cellulose is effected by aërobic organisms, of which several have been isolated, including the rather remarkable organism, *Spirochæta cytophaga*, isolated from Rothamsted soil by Hutchinson and Clayton. Little is known with regard to the organisms responsible for the breakdown of pentosans and of lignin, nor have we yet any definite idea of the course of the decomposition of these complex materials. It is tolerably certain that the first stages of the breakdown of most complex plant materials are biological in nature, but whether the subsequent formation of humic matter is brought about by biological or by purely chemical agencies is uncertain.

Reference may here be made to the existence in the soil of a remarkable group of bacteria which are able to oxidise elementary sulphur to sulphuric acid, and to withstand considerable concentrations of that acid. This subject has been extensively studied by Lipman and his co-workers at New Jersey, and the process is being applied in practice as a means of changing the hydrogen-ion concentration of the soil for certain specific purposes, such as the control of the potato scab disease, the reclamation of " black alkali " land, and the rendering soluble of mineral phosphates.

Until the year 1909, the soil bacteria had almost completely monopolised the attention of soil biologists, and although other micro-organisms—protozoa, algæ, fungi—were known to be present in the soil, their importance in soil processes had scarcely been considered. In that year, however, the non-bacterial soil population was brought into great prominence by the work of Russell and Hutchinson on the " partial sterilisation " of the soil. This work arose out of the earlier work of Darbishire and Russell on the oxidation processes in soil. The absorption of oxygen and the production of carbon dioxide are largely a function of the biological activity in the soil, and were used by Russell as a means of correlating the latter with the

fertility of the soil. As has so often happened in scientific investigations in the past, an apparent anomaly in the results, arising from an accident, gave the clue to an entirely new conception of the nature of the biological phenomena in the soil. It was found that if the soil was heated to 100° C., or was treated with an antiseptic, the initial fall in bacterial numbers was succeeded

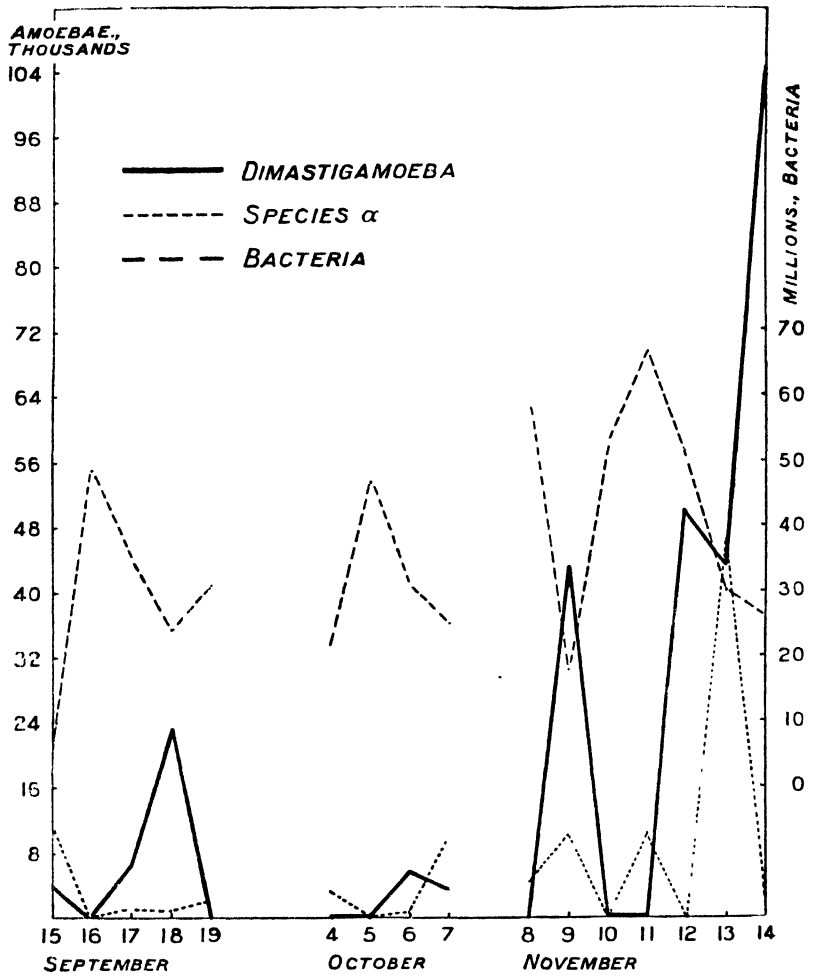


FIG. 3.—Numbers of active amœbæ (Dimastigamœba and Species α) and bacteria in 1 gram of field soil for typical periods in September, October and November 1920 (D. W. Cutler, L. M. Crump and H. Sandon).

by a rapid rise, which soon reached a level very much higher than that normally obtaining in the untreated soil; the production of soluble nitrogen compounds was correspondingly enhanced, with the result that soil treated in this way was much more fertile than before. It was therefore concluded that in normal untreated soil there is present some factor which keeps down the numbers of bacteria; from a careful study of the conditions governing the destruction of this limiting factor and its reappearance in the soil, the conclusion was drawn that this limiting

factor was biological in nature. Russell and Hutchinson's hypothesis was that this biological factor consists of protozoa, which were known to occur in soil; moreover, active protozoa were known to feed on bacteria. In the process of partial sterilisation all the protozoa were killed, so that when the bacterial spores (which are not killed by the partial sterilisation process) germinated, the bacteria were able to flourish and multiply in the absence of the protozoa to such an extent that they reached much higher numbers than in their presence. The hypothesis was supported by the fact that protozoa could not be found in partially sterilised soil, but if they were reinoculated into such soil, the bacterial numbers again fell.

A detailed study of the soil protozoa was therefore commenced, and is still in progress. Before the War this work was undertaken by Goodey and by Lewin, and after the War it was resumed by Cutler. Active protozoa have been shown to be normal inhabitants of the soil, and methods for their enumeration in the soil have been worked out. The numbers of bacteria and of six different species of protozoa were determined in daily samples of soil from Barnfield at Rothamsted for 365 consecutive days. When the results were plotted it was found that there was a striking relation between the numbers of bacteria and of active amœbæ. When the bacteria were numerous the active amœbæ were relatively scarce, and *vice versâ*.

These results thus afford strong evidence in favour of the truth of Russell and Hutchinson's hypothesis.

The study of the green algæ of the soil has been in progress for a shorter time than that of the protozoa. Little definite evidence has yet been obtained with regard to their function in the soil. Methods have, however, been worked out for growing them in pure culture, entirely free from bacteria and other organisms, and they are being studied with special reference to their bearing on the nitrogen cycle in the soil. The possibility of their being able to assimilate atmospheric nitrogen was recently investigated by (Miss) Bristol and the writer, an American worker having claimed to show that they were able to do this. Bristol and Page could find no evidence for the fixation of nitrogen by green algæ, and at present they are being studied from the point of view of their relation to the fixation of nitrogen by soil bacteria and to the assimilation of nitrate in the soil, since it seems not unlikely that they may play an important part in the assimilation of nitrates discussed on p. 234.

Fungi are very plentiful in the soil. They are known to be capable of the ammonification of organic nitrogen compounds and of breaking down complex carbohydrates such as cellulose. Little more than a beginning has, however, yet been made in their study, and it is not yet possible to say how great is their share in biochemical soil processes.

Before leaving the subject of the biochemical changes in the soil, reference may be made to another direction in which partial sterilisation has led to an increase in our knowledge of the activities of the soil bacteria. It is found that when organic antiseptics such as phenol, toluene, naphthalene, are added to the soil, they fairly rapidly disappear, and a search for the cause of this disappearance has revealed the existence in the soil of a number of groups of bacteria which are able to decompose these aromatic substances and to utilise them as sources of energy. When it is remembered that phenolic constituents are present in appreciable amounts in herbivorous urine, it will be seen that in the absence of organisms of this type there would be a tendency for the accumulation of these products in the soil in toxic quantities. There is, however, in addition to a biological oxidation of phenol, a purely chemical one, dependent on the presence of manganese in the soil.

It will thus be seen that the soil population is a very complex one, and that the chemical

and biochemical processes in the soil exhibit manifold inter-relationships, the elucidation of which presents innumerable fascinating problems. The attached diagram is an attempt to represent, in schematic form, the present state of our knowledge of the chemical and biochemical changes in the soil.

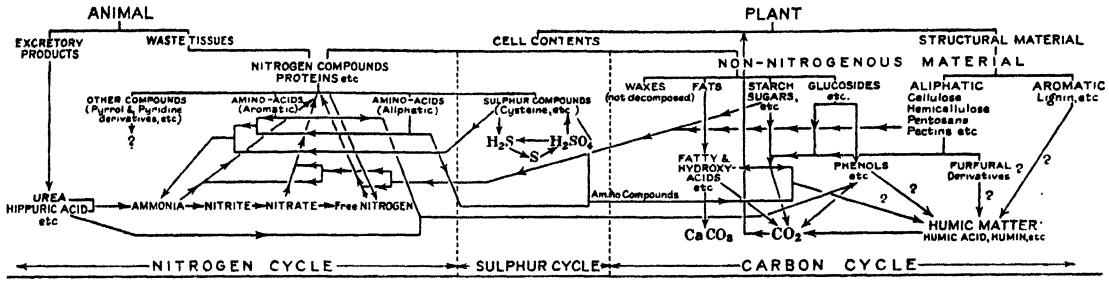


FIG. 4.

The part played by plant diseases as a factor in the control of crop production calls for discussion in this article only in certain special directions. The control of fungus and insect pests by spraying with fungicides presents many chemical problems, and considerable attention is being devoted to the possibility of utilising synthetic organic products for this purpose, more

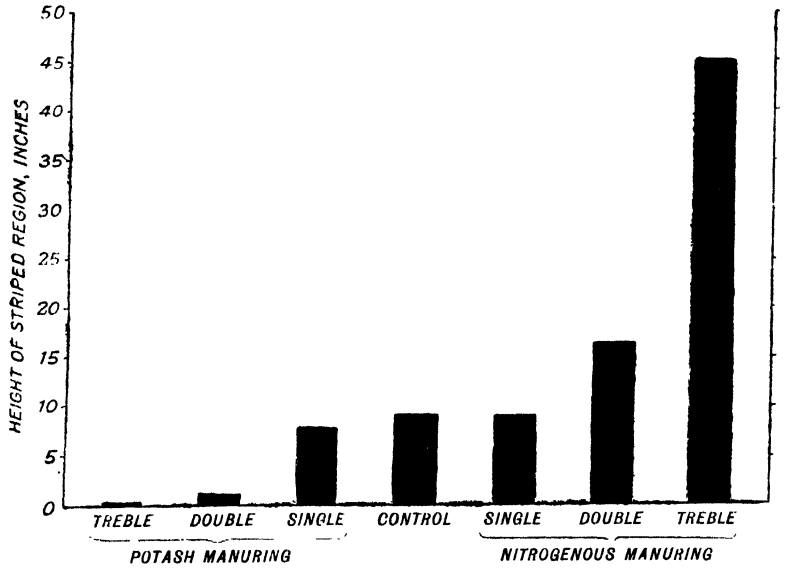


FIG. 5.—Influence of potash and nitrogenous manuring on the degree of infection of tomatoes by bacterial stripe disease (W. F. Bewley).

particularly as insecticides, in place of natural substances such as nicotine, which are relatively scarce and expensive.

The effect of fertilisers on the incidence of plant disease is another aspect of the subject in connection with which interesting results have been obtained. Quick-acting nitrogenous

fertilisers such as sodium nitrate are often of great value when a crop is seriously infested in its early stages with an insect pest, by stimulating rapid growth so that the crop "grows away" from the attack. The soft sappy growth induced by too much nitrogenous manure, however, renders plants particularly susceptible to fungus and bacterial disease; potash manures, on the other hand, have a marked effect in imparting vigour to the plant and in increasing its power of resisting disease. This is well illustrated by some experiments on tomatoes carried out by Bewley, the results of which are shown in Fig. 5.

Much of the work that has been discussed in this article is at present of importance chiefly in its bearings on the elucidation of the underlying principles of agricultural chemistry. On the other hand, many of the other investigations that we have dealt with have obvious practical applications that need no further comment here. Special reference must, however, be made to two subjects of great practical importance. One of these, the partial sterilisation of the soil, has already been dealt with in its theoretical aspects. The

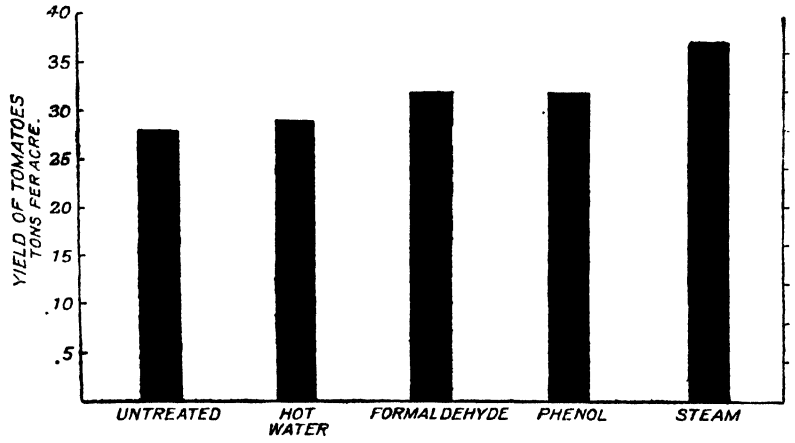


FIG. 6.—Effect of partial sterilisation of greenhouse soil on yield of tomatoes. Average of results for 5 years (1919–23) (Cheshunt Experimental Station).

practical application of partial sterilisation has met with very great success in the glasshouse industry, in which it now figures almost as a standard process of soil treatment. The crop increases which are brought about by the treatment of the soil with steam or organic antiseptics are considerable. Fig. 6 illustrates the results that have been obtained by the use of steam, formaldehyde, and carbolic acid in large-scale trials carried out at the Experimental Station at Cheshunt. The partial sterilisation process is a complex one, and at least four different factors are now recognised as contributing to its effect. In the first place, there is the removal of the biological limiting factor, the protozoa, with the resulting increase in bacterial activity and in the biochemical production of plant food. This has already been discussed on p. 236. Secondly, there is the direct liberation of plant food from the organic matter of the soil by the action of heat or antiseptics, which was demonstrated by Pickering and others. Thirdly, there is the feeding effect of the organic antiseptics themselves on the soil bacteria, which has been referred to on p. 237. In the case of heat treatment, the soluble organic substances liberated by the treatment probably act in a similar way. Finally, there is the effect of the treatment in killing

off plant disease organisms, such as nematodes. The relative importance of these four factors necessarily varies from case to case, according to the nature of the soil and of the factor which is limiting plant growth in that soil before treatment.

The other important practical advance to which special reference is needed is the process worked out at Rothamsted for the manufacture of synthetic farmyard manure. The shortage of animal manure is every day becoming more and more acute, and there is a real need for some alternative means of adding to the soil the organic matter which is of such importance for the maintenance of soil fertility. The shortage of farmyard manure arises, not from any shortage of straw, but from a shortage of animals, caused in no small degree by the replacement of the horse by mechanical traction. Earlier work at Rothamsted by Hutchinson on the

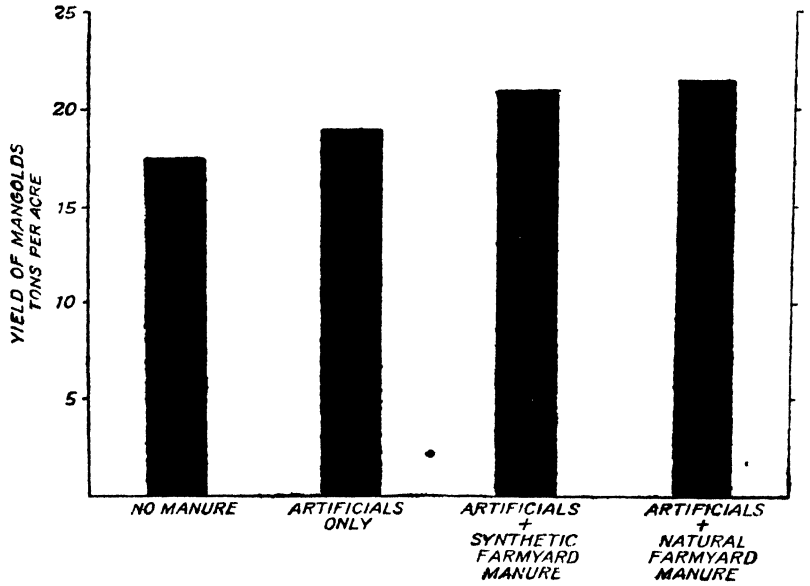


FIG. 7.—Comparative effect of synthetic and natural farmyard manure on the yield of mangolds (Wye Agricultural College, 1922)

breakdown of cellulose in the soil and on the relation of carbohydrate material to nitrogen fixation and nitrate assimilation (see p. 234) led Hutchinson and Richards to study the conditions under which straw could be caused to rot down. As a result of this work, they found that by treating wet straw with a certain amount of combined nitrogen and maintaining the reaction of the mixture faintly alkaline it was possible to convert the straw into a product which had all the outward appearance of farmyard manure and was of very similar composition. Field trials gave very promising results, and the process was patented. The commercial development of the process is now in the hands of the Agricultural Development Company, a non-profit-making syndicate which owes its origin to the public-spirited action of Lord Elveden, who had already given considerable support to the earlier work on which the process is based. The process has now been further improved in several respects, and a number of large-scale trials have taken place in various parts of the world. The results of a recent field experiment carried out at Wye are shown in Fig. 7. In this country straw is the raw material to

which the process would ordinarily be applied, but many other waste plant products from outlying parts of the Empire have been tested and successfully converted into synthetic farmyard manure in the laboratory. The further development of this process promises to be of great value to agriculture both in this country and overseas.

Finally, our survey of the present position of agricultural chemistry may be completed by a brief review of some of the other present-day problems, the detailed discussion of which is not possible in the space available. The importance of organic matter to the soil has been emphasised repeatedly in this article, and the value of farmyard manure and of its synthetic substitute for this purpose has been indicated. Other methods of adding organic matter to the soil are (1) the growth of clover and other leguminous crops such as lucerne, and (2) the use of green manures, that is, the growing of green crops specially for the purpose of ploughing them under. In both these methods many problems arise in which the agricultural chemist is directly concerned. Another problem of first-rate practical importance is that of the quantitative relation between the amount of fertiliser used and the amount of crop increase obtained. Further, there is the question of the relative value of the many different varieties of artificial manure now available to the farmer. In the case of the nitrogenous artificials, there are, in addition to ammonium sulphate and sodium nitrate, several products derived from the various nitrogen-fixation processes now in operation. Calcium cyanamide, or "nitrolim," which was first produced commercially in 1904, has had rather a chequered career, and it does not appear to have a great future as a fertiliser. It is, however, likely to find extended use as an intermediate substance for the manufacture of ammonium salts and of urea; the latter substance has given promising results, and may ultimately figure as an important fertiliser. Calcium nitrate is another synthetic product, first produced by the Birkeland-Eyde process in Norway in 1905, and is a very valuable manure, finding a ready sale, although it is doubtful whether it will be able to compete with other products derived from cyanamide or from the synthetic ammonia processes of Haber and Claude. Among phosphatic fertilisers, superphosphate, basic slag, and bone manures are in general use, and the relation of soil and climatic conditions to their relative value and to the value of ground mineral phosphate is a problem of great practical importance and is being studied at the present time. Similarly, in the case of potash manures, the development of the Alsatian potash deposits, which consist wholly of chlorides, has necessitated a critical enquiry, which is now in progress, into the relative value of chloride and sulphate of potash as manures.

Fertilisers have been studied in the past mainly with regard to their effect on the yield of crops, and the question of quality has received but little attention. This question is now being specially investigated with two crops, potatoes and malting barley. The latter crop is a particularly suitable one, for the relation between the quality of barley and that of the resulting malt is a subject of great importance in the brewing industry, and the possibility of correlating the results of field trials and of chemical examination of the barleys and malts with the accumulated experience of maltsters and brewers is an attractive one.

In this brief account it has scarcely been possible to do more than touch on the fringe of the subject, and to give a few glimpses of the nature of the many fascinating problems presented by the chemistry of the soil and of crop production. Perhaps more than most "borderland" subjects, this is one in which the inter-relations of the many factors involved and the complexity of the problems presented are such as to give rise sometimes almost to a feeling of despair that order will ever come out of the chaos and welter of conflicting views and apparently conflicting

facts. Progress of knowledge in a borderland subject necessarily lags behind that in its associated pure sciences, on which it is dependent for the implements used in the attack of its own special problems. Looking back on the state of agricultural science at the commencement of this century, we have, however, no cause to be dissatisfied with the progress that has been made, nor with the part that British investigators have played in that progress; moreover, the present position of the subject appears to justify the belief that future progress will be no less rapid, and the Empire's part in that progress no less great, than it has been in the past.

ALLOYS

By C. H. Desch, F.R.S.

Whilst it may be admitted that until the close of last century the manufacture and application of non-ferrous alloys, as well as their scientific study, lagged far behind those of steel, great advances have been made during the last twenty-four years, and in those advances, both technical and scientific, British metallurgists have taken a prominent part. The industry has grown and has become more varied to meet the increasing requirements of the engineer, every new development in engineering having called for improvements in existing alloys or the invention of new alloys. For instance, the invention of the steam turbine made it necessary to find alloys capable of resisting the impact of steam jets at high temperatures and moving with high velocities, a need which led to a marked improvement in this direction. The most noteworthy impetus to research has been given by aeronautics. The development of the aeroplane and of the airship has made both necessary and possible the production of light alloys of considerable strength and resistance to fatigue, some of which, used as pistons in internal combustion engines, must have the further properties of good conductivity for heat and chemical resistance to hot gases. These requirements could not be met from the resources of metallurgy of a quarter of a century ago.

Light Metal Alloys.—The solution of the problems just named has been made possible by the use of the light metal aluminium. Although one of the most abundant of the metals in combination with other elements in minerals, the difficulties of extraction are such that it was not until 1887 that the introduction of the electric furnace into the industry made its manufacture on any considerable scale possible. It has now become one of the most familiar metals, and is manufactured wherever cheap electrical energy can be obtained from water-power. Pure aluminium, however, is a weak metal, yielding unsatisfactory castings, and it must be alloyed in order to make it useful for engineering. In 1910, a new alloy, duralumin, was introduced into this country, having excellent mechanical properties due to the addition of copper with a small quantity of magnesium. This alloy increases in strength on " ageing," a property which has only recently received an explanation. Alloys of aluminium and zinc were found to make good castings, and have been largely used for such objects as motor-car crank cases. The further development of light aluminium alloys has been influenced by the growth of aeronautics, especially during the War, and has been largely due to work undertaken for the Air Ministry at the National Physical Laboratory and the Royal Aircraft Factory. Great strength, even at high temperatures, has been obtained by adding nickel, or sometimes manganese, to these alloys, and the Eleventh Report to the Alloys Research Committee, published in 1921, contains a remarkable record of successful alloys, for use as castings or in the forged or rolled condition, most of the early difficulties having been overcome. The new alloys of aluminium and silicon have very valuable properties.

The improvement of these alloys by suitable heat treatment has become an important branch of practice in the industry, and a scientific explanation of the effects has been arrived at by careful research at the National Physical Laboratory. The changes are proved to be due to the passage of certain compounds, chiefly magnesium silicide, into and out of solid solution in the main constituent, the maximum hardness being produced when the compound in question has separated from solution in a state of very fine dispersion.

A lighter metal even than aluminium, and one which is also abundant in nature, is magnesium, with a specific gravity of only 1·74, and in the last few years alloys of magnesium have been introduced into the engineering industry, especially for motor-car work. In spite of the inflam-

mable nature of the metal and its low melting point, it has been found quite practicable to make pistons for internal combustion engines and moving parts for such light machines as typewriters from alloys composed mainly of magnesium. Another extremely light metal, beryllium, with a specific gravity of only 1·8, has the advantage of a very high melting point, and although it is at present classed among the rarer elements, it is quite possible that in this, as in other instances, a demand for the metal may lead to the discovery of new sources of its ores, and experiments are in progress to determine which of its alloys offer the greatest prospects of usefulness.

Most light alloys are liable to corrosion, and this is their most serious defect at present. Much research is being directed to this problem, in the direction of increasing their resistance to corrosion by changes of composition, or of giving them protection by means of suitable coatings.

Die-casting Alloys.—The alloys of aluminium are among those which are most frequently used in the rapidly growing industry of die-casting. By forcing a molten metal under pressure into metal dies, either by means of a plunger or by the use of compressed air, and removing the casting as soon as it is solid, it is possible to cast objects of very varied and often complicated shapes with such accuracy of size and such smoothness of surface as to render machining unnecessary. In this way, an extraordinary variety of objects, which would formerly have been machined out from the solid or built up of smaller parts, may be manufactured as simple castings, at very much lower cost. It is particularly in the motor-car industry that light aluminium alloys are cast in this way. For other purposes, die-castings are largely made of alloys containing zinc as their principal constituent, and these include cog-wheels, etc., so that such an instrument as a penny-in-the-slot gas meter, with its enclosing case and mechanism, can be constructed entirely from die-castings, which only require to be assembled. White metals for bearings, etc., are conveniently die-cast to shape. The application of the process to brasses and bronzes is more difficult, owing to the high temperature of the molten metal and its action on the dies, but even in this direction great progress has been made, and the process has proved useful in the construction of dynamos and other electrical machinery. It is likely to be more widely employed in the near future, when the difficulties of making sufficiently resistant dies have been overcome.

Brasses and Bronzes.—The manufacture of brasses and bronzes has undergone comparatively little change in the period under consideration. The introduction of new alloying constituents, such as vanadium, has been tried, but without any remarkable results, and the striking success of alloy steels has not been repeated in the non-ferrous industry. There still remains, however, a wide field for experiment in this direction, and systematic exploration may lead to valuable discoveries. Special attention had to be given during the War to two varieties of brass, the 70 : 30 alloy used for cartridge cases, and the approximately 60 : 40 alloy which is the principal material for shell fuse bodies. Cartridge brass has to be severely cold-worked in making the finished cases, and the necessary ductility can only be obtained by giving attention to the purity of the metals and to the care taken in casting. Practice in the brass casting shop has been improved in consequence. The alloy for fuse bodies must have good machining properties, as it has usually to pass through automatic lathes, and here again purity has been found to be important, the presence of iron, aluminium, or oxides of any kind producing hardness. Extruded rods, rolled rods, and hot stampings were used, and experience showed that the texture of the metal, that is, the arrangement of the α- and β-constituents, as well as its chemical composition, was of importance.

Certain defects which appear in brass in the course of use have been the object of study. Brass condenser tubes are liable to corrosion, and much loss and inconvenience are thereby caused

to shipping and also to power stations on land. The failures are erratic, some waters having a much greater effect than others and some tubes in a condenser being rapidly corroded whilst neighbouring tubes are quite unaffected. The seriousness of the matter led the Institute of Metals to appoint a special Corrosion Committee, on which the manufacturers, the Admiralty, the marine engineers, and scientific metallurgists are represented, and the research staff of this Committee has issued a number of reports in which the principal factors in corrosion have been identified, and means of lessening its extent have been indicated, although the complete solution of the problem has yet to be found. Whilst the mass of facts concerning corrosion is vast and indeed overwhelming, the theory of the subject is in an unsatisfactory position, although everything now goes to confirm the electrolytic conception of the phenomenon.

Another defect to which brass, in common with some other alloys, is liable is season-cracking. Cartridge cases, hard-drawn tubes and wires, and other severely cold-worked objects may crack some time after manufacture, especially if exposed to a corrosive atmosphere, such as air containing traces of ammonia. A change of temperature, as on entering the tropics on a sea voyage, may also cause cracking. Work at Woolwich Research Laboratory has shown that the danger of season-cracking may be removed by a process of annealing at a low temperature (from 200 to 300° C.), the heating being sufficient to relieve internal stresses, but not to soften the hardened metal. This result is of great importance, and has had a marked effect on the non-ferrous industry, in which cold pressing, drawing, spinning, and similar processes are so largely employed.

Nickel Alloys.—Cupro-nickel is an alloy remarkable for its capacity for undergoing severe cold working without cracking, but this property depends upon the freedom of the alloy from non-metallic inclusions. In its preparation, care has to be taken to avoid the presence of oxides on the one hand or of graphite on the other. The demand for cupro-nickel for bullet sheathing during the War made it necessary to instruct men in the precautions to be taken in its manufacture, and this instruction was provided in the University of Sheffield. The experience gained in connection with cupro-nickel has proved useful in the metallurgy of nickel silver, the alloy so widely used as a basis metal for electro-plating. Monel metal, the alloy of copper and nickel obtained directly by smelting the ore of Sudbury, Ontario, has proved its value for engineering purposes, and in particular resists well the action of sea-water. It has been extensively used, both as castings and in the forged or rolled condition, and it has been found worth while to manufacture a similar alloy in this country from metallic copper and nickel. Alloys of this class will probably find wide application in the future.

Many of the new alloys which resist corrosion in an unusually high degree contain nickel as one of their components. The alloys of nickel and chromium, which may also contain iron, are remarkable for their chemical inertness, not only in contact with corrosive substances at ordinary temperatures, but also in air and other gases at a red heat. For this reason they are used in place of iron or steel for annealing and case-hardening boxes, and have the great advantage of not becoming warped when kept in the furnace for long periods. When, for the purposes of a process for the synthesis of ammonia, vessels were required which would resist enormous internal pressures (up to 900 atmospheres) for months at a temperature of 600° C., these alloys were found to be far superior to steels, as they are less liable to viscous flow under continued load. The alloys are very difficult to forge in large masses, so that for such vessels castings have to be used, but by reducing the mass and slightly varying the composition, malleable alloys are obtained, which, when rolled into strip or drawn into wire, find application as resistances in electric furnaces

or domestic heaters. As the proportion of iron in the alloys is increased, they merge gradually into the class of stainless steels.

The very high melting point of one of the compounds of nickel and aluminium is the reason for the introduction of aluminium into some of these complex alloys employed for work at high temperatures.

Turbine Blade Alloys, etc.—The properties of the ductile alloys at high temperatures are of interest to designers and builders of steam turbines and other machines, parts of which are exposed to hot air or superheated steam. Phosphor bronze has been largely used for turbine blading, but has now to compete with the newer alloy steels. The resistance of a metal to erosion by a current of steam at high velocity cannot be inferred from a study of the material at atmospheric temperatures, and the experimental procedure is difficult, but much useful information has been obtained from researches in Glasgow and Birmingham, and from records of observations in the marine engineering and railway locomotive shops.

Silver Alloys.—The tarnishing of silver is a special case of corrosion, of much practical interest, especially in large towns, where the air always contains sulphur compounds. A sterling silver which is less liable to tarnish than the usual alloy has been brought into commerce, the copper being replaced by other metals. The actual composition has not been made public and research is in progress. In this connection, the useful work of the Atmospheric Corrosion Committee may be mentioned. Many factors are involved in the tarnishing and corrosion of metals exposed to moist air or to air laden with fumes and products of combustion, and their separation and study afford a difficult problem. It should be noted that very thin films formed by oxidation may protect against further corrosion.

Cobalt Alloys.—Cobalt, a metal which has come into increased prominence owing to the working of extensive deposits in Canada, has provided some important alloys in addition to the cobalt steels. Alloyed with chromium and tungsten, it forms stellite, a very hard alloy which replaces high-speed steel as a material for turning tools for certain classes of work.

Heat-treatment of Non-ferrous Alloys.—The remarkable results obtained from the light alloys of aluminium have drawn attention to the possibility of improving the properties of non-ferrous alloys by suitable heat-treatment. Whilst it is unlikely that many alloys will undergo, when quenched, such an astonishing change of properties as is familiar to us in hard steel, it is certain that the brasses, bronzes, Britannia metal, and other alloys in general technical use may often be improved in strength or ductility or toughness by subjecting them to a thermal treatment based on their known equilibrium diagram. This procedure, although not yet widespread, is gradually becoming more common, and in this, as in several other matters, the non-ferrous alloy manufacturer may well take a hint from the steel-maker, and base his practice more directly on the results of scientific investigation.

Research on the Constitution of Non-ferrous Alloys.—The study of alloys by means of the microscope, founded on the early work of H. C. Sorby on steel, has become general during the period under discussion, largely owing to the work of Heycock and Neville at Cambridge. It was in 1902 that these authors, who had previously determined with great accuracy the freezing-point curves of a large number of alloys, published their important investigation of the copper–tin series, a difficult group, to study which they used the microscopical method combined with the newly-devised method of quenching from carefully determined temperatures, and finding by interpolation the actual temperatures of transformation. Interpreted in the light of the new physical doctrine of phases due to Willard Gibbs, then coming to recognition mainly owing to the

theoretical work of Roozeboom, this work provided a firm basis for the metallography of alloy systems. Very accurate experimental methods have been devised at the National Physical Laboratory, where many alloy systems have now been investigated, and elsewhere. It has been found that most binary alloy systems are more complex than had originally been supposed, and that polymorphic changes and variations of solid solubility with temperature are the rule rather than the exception, so that much work will be required to establish the true equilibrium diagrams. The conditions in ternary systems are more complicated, but steady progress is being made in their study, the data obtained being plotted on a tetrahedral model. The number of individual observations necessary for the construction of such a model is very large.

Much attention has been devoted to the subjects of cold-working in metals and the crystallisation and grain growth which follow the annealing of cold-worked metals. The theory of the process is still imperfect, but the observations are of extraordinary interest. Light has been thrown on the problem by the discovery by Carpenter and Elam that very large crystals may be produced in pure aluminium by straining to a certain critical amount and then annealing. In this way, a test-piece may be brought to consist of a single crystal, on which mechanical tests may be made. Such large crystals have remarkable properties, and their behaviour makes it possible to interpret in a new way that of masses composed of an aggregate of crystals, as are technical metals and alloys. The mechanical behaviour of a metallic mass is the resultant of two sets of properties, those of the individual crystals and those of the intercrystalline boundaries. Single crystals prepared by the method just mentioned or by that due to Czochralski, in which a growing crystal is withdrawn from the liquid at a rate corresponding with the velocity of crystallisation, may now be studied separately. The boundary still remains an obscure factor. In it probably reside the property of elastic after-working, which appears to be absent from single crystals, and much of the resistance to deformation under stress. The view that adjacent crystal grains are united by an amorphous layer, in which the atoms are not arranged on a definite space lattice, has been ingeniously used by Rosenhain and others to explain a variety of effects, including season-cracking, the variation of tensile strength with temperature, and viscous flow under steady load, but it is open to theoretical objections. On the other hand, it has been shown that the crystal grains have forms approximating to those of foam cells, and therefore determined by surface tension, and it seems likely that further study of the surface tension of solids, the experimental determination of which is a difficult problem, will go far to clear up the obscurity.

The effect of the dispersion of one solid phase in another has been mentioned above in connection with the ageing of alloys of aluminium. When a constituent separates from a solid solution on cooling, the molecular aggregates are at first small, and their subsequent union to form particles of microscopic size closely resembles the flocculation of a colloid. Whilst it is going too far to reduce the study of such processes to a department of colloid chemistry, as has been proposed, it is certain that an investigation of the effects of surface tension on a dispersed solid phase will prove interesting. There is obviously no electrolytic effect such as is important in ordinary colloidal systems.

***X*-Ray Investigation of Alloys.**—The scientific study of metals and alloys has been powerfully assisted by the new developments in the method of analysis by *X*-rays. The methods of Bragg, Debye, and Hull, unlike the original method of Laue, lend themselves to the examination of aggregates of crystals, whilst the systematic *X*-ray examination of single crystals during deformation has yielded most interesting information. It is now clear that the greater hardness

of solid solutions as compared with their component pure metals is due to distortion of the space lattice, and increases with the amount of that distortion. The plastic elongation of a sheet or wire is accompanied by a swinging round of the crystal planes along which slip occurs most readily into a position more nearly parallel to the direction of elongation, and a severely cold-drawn wire has a distinct fibrous structure, very similar to that of natural fibres such as silk or cotton. In this connection, reference may be made to the remarkably high tensile strength of rods of fused silica, drawn under such conditions as to give a parallel direction to their molecules. The theory of Beilby, that severe deformation is always accompanied by a local breaking down of the space lattice, although rejected by some Continental workers, is generally accepted in this country, and serves to correlate the facts of plastic deformation in a remarkable manner. Anomalous results are still obtained in the investigation of the fatigue of metals, but in this field research is very active, and here again one factor may be eliminated by studying the behaviour of single crystals. These crystals, in spite of their very low " elastic limit," have a definite and fairly high " fatigue limit." The increasing use of machines running at high speeds has given great importance to the subject of fatigue, whilst the turbine and the internal combustion engine are responsible for the work now in progress on the fatigue of metals at high temperatures.

A further application of the *X*-ray method is to the study of the constitution of alloys. The alloys of copper and zinc, for example, have been examined recently by Owen and Preston, and it has been possible to show how the successive solid phases, although crystallographically different, are formed from one another by simple deformations of the space lattice. A controversial point, as to whether the change of the β-brasses at 470° is due to the resolution of a solid solution into two phases or to a polymorphic change like that of β- into α-iron has been definitely decided by the *X*-ray method in favour of the latter view. This method is likely to be resorted to widely in the future.

In general, it may be said that the scientific study of alloys is making rapid progress, and that it represents one of the most interesting applications of physics and chemistry to a subject of great industrial importance. Whilst many improvements have been made on the technical side, it is certain that the main advance comes from research in pure science, and that it is the metallurgist who has received a scientific training firmly based on physics and chemistry in whose hands rests the future of the alloy industry.

POTTERY AND REFRACTORIES

By Joseph Burton

The first quarter of this century has seen many important developments in the Pottery Industry of this country, not only by way of improvements in existing processes, but also in the introduction of new methods both in the making and the firing of ware. A vast amount of research work has been carried out by workers in various parts of the country, but it has mainly centred round Dr. J. W. Mellor, Mr. Bernard Moore, and the Ceramic Society at the Central Pottery Schools, Stoke-on-Trent. The Chemistry of the Pottery Industry is the Chemistry of arrested action, and the chemical changes that take place in the firing or baking processes are difficult to follow and to determine with precision. The " bodies," glazes, and colouring materials used are mixtures of complex compounds, of which the chemical constitution is in many cases a matter of guesswork in the present state of our knowledge, but much systematic work has been done in connection with the chemical and physical changes that take place in every stage of the firing processes, and present-day practice is based largely on the knowledge so obtained.

The white earthenware " body " made in this country—where this type of pottery " body " originated—consists of an intimate mixture of ball clay, china clay, calcined flint, and Cornish stone. Each material has its own function in the " body," and it is important that standard conditions of composition, mixing, and method of preparation be maintained. Since chemical action between the particles can only take place at the points of contact, the size of the particles of the materials used has an important bearing on the quality of the ware, both after the first or " biscuit " fire and after the second or " glost " fire. The materials are mixed together in suspension in water. The clays are stirred about with water until they break down into their natural fine state of sub-division which the potter cannot alter, but the calcined flint and the stone are ground in water to the degree of fineness required. Flint, which, as used, contains approximately 96% of silica, acts as a powerful acid anhydride at the temperature of the pottery oven, and it is the most active ingredient of the body, so that the size of the particles of flint is of extreme importance.

Experimental body-building with ground flint of different degrees of fineness as determined by elutriation tests, and the determination similarly of ground flint as used in bulk on many factories, have established a certain standard size of particle—often stated as " surface-factor "—which will give the best results. The size of the flint particles has a determining influence on the " crazing " and of the " peeling " of glaze, and it is the current practice on well-conducted pottery works to carry out frequent—generally daily—elutriation tests of the ground flint so that a reasonable degree of constancy shall be maintained in this respect.

The ground flint as used always contains a small percentage of lime, and the effect of this on the fired body is of interest. In the first place the lime acts as a bleaching agent on the iron compounds in the body—therefore producing a ware of better colour—but if the percentage of lime is increased there will be a greater tendency towards " crazing " of the glaze unless the composition of the body and the firing temperature of the biscuit oven be adjusted.

The mixture of body materials and water commonly known as clay-slip is now generally passed through a trough containing a system of electro-magnets which remove the metallic and magnetic iron which would otherwise slightly discolour or speck the ware.

The action of the chemically combined water in clay during the firing process has received much attention. Clay substance, or the essential clay basis of natural clays, which are always mixtures of various mineral substances, may be assumed to have the empirical composition

$Al_2O_3,2SiO_2,2H_2O$. This compound remains apparently unaltered during the early stages of the firing, but at a temperature of about 500° C. the water is liberated and passes away as vapour. This high-temperature water vapour may react chemically with some of the incidental ingredients of the body (such as the iron compounds), but in any case the steam if evolved rapidly will completely envelop the ware and push back the ordinary oxidising atmosphere of the oven, and may so produce undesirable and harmful conditions. All clays contain more or less carbonaceous matter, and at 500° C. most of this remains as finely divided carbon. If the water-vapour prevents the ready access of oxygen, this carbon will remain unburnt until a comparatively high temperature has been reached, during which period it will exert a strong reducing action on the iron compounds which are always present in the body. It has been conclusively proved that the black core often found in bricks, the flashing or staining and certain specking effects of tiles, and similar results are due to the combined action of the water-vapour (when rapidly evolved), carbon, and iron compounds, and, further, that if the combined water be liberated slowly and gradually the vapour passes away with the oven gases without exerting any undue influence, and no ill effects follow. Present practice in firing ensures this slow elimination of the water by a retarding of the firing between 500° C. and 700° C. In this way most of the carbon is also burnt out at this comparatively low temperature.

Many variations of body composition have been introduced in recent years for the manufacture of earthenware of special qualities. The proportion of the more fusible ingredient, Cornish stone, has been increased, and in some cases a percentage of felspar added to produce a stronger and more vitreous ware approaching a fine white stoneware, and generally the quality of the earthenware made in this country is maintained at the highest level and remains one of the finest pottery wares for general domestic use in the world.

Pottery ware based on English earthenware is now being made in many other countries, and it is only by the application of the scientific knowledge obtained in the research laboratories that this country can hope to hold its pre-eminent position.

The ordinary English bone china body—another indigenous product—consists of an intimate mixture of calcined bone, Cornish stone, and clay. It is probably the most chemically complex of all pottery bodies, and has been made the subject of much research work. In 1905, Mr. Bernard Moore read a very important paper before the Ceramic Society on "The Cause and Prevention of Brown Coloration of China in the Enamel Kiln." The ware, although apparently sound and good after the biscuit and the glost firings, becomes discoloured in patches by a brown stain which appears in the final firing of the decorated ware in the enamel kiln. Mr. Moore suggested that this was due to the oxidation in the enamel kiln of ferrous phosphates formed in the body under certain conditions of firing in the biscuit oven, and he pointed out that this defect had gradually appeared in increasing quantity during a period of years in which certain alterations in the quality of the Cornish stone and the percentage of clay had been introduced, and, further, that these alterations, which resulted in a lowering of the percentage of the alkalis in the body mixture and an increase in the percentage of alumina, were directly responsible for conditions favourable to the suggested chemical changes. The publication of this research produced immediate practical results and has undoubtedly been of very great value to the China industry, saving constant and considerable loss. The somewhat related defect of "spit-out" which often occurred in the enamel kiln was also investigated at the same time, and shown to be due to the sudden blowing out of gas (mainly of water-vapour) from the body. Both ferrous phosphate and phosphoric anhydride—which may be present in bone

china biscuit under certain conditions of biscuit firing—have a great avidity for water, and if the enamel firing is conducted at too rapid a rate, this absorbed water will be blown out as vapour so suddenly and with such force that it breaks away a portion of the glaze and causes "spit-out." Dr. Mellor has shown that the bloating of over-fired china biscuit was due to the liberation of phosphorus from the bone ash by the action at high temperatures of the silica of the Cornish stone, an action which is facilitated by the presence of carbon or of a reducing atmosphere during the later stages of the firing. The formation of ferrous phosphate is also due to the combined action and reaction of the silica, bone-ash, and iron compounds in a reducing atmosphere.

In 1916, the Board of Industrial and Scientific Research built and equipped a pottery laboratory adjoining the Central Pottery Schools at Stoke-on-Trent, and they appointed Mr. Bernard Moore and Dr. Mellor to conduct a research on hard-paste porcelain. Hard-paste porcelain is essentially a German product, and the body mixture consists of orthoclase felspar, clay, and quartz, in such proportions that a high firing temperature (in the neighbourhood of 1400° C.) is necessary to produce the characteristically dense and vitreous ware. The English chemists finally produced a fine hard-paste body, using British raw materials only, and at the same time they obtained a mass of valuable information in other directions, such as the properties of the fireclays of various compositions used for making the "saggers" in which pottery ware is fired, the preparation of glazes for high temperature firing, etc. This important research has had direct and indirect practical applications and will be increasingly fruitful in the next few years.

The electric-fittings branch of the industry has shown considerable developments especially in the manufacture of insulators for high tension work. The tendency has been towards bodies having a higher percentage of felspar and clay and fired at a higher temperature—bodies which more nearly approach hard-paste porcelain. Sparking-plug bodies are now very largely made; they contain a large percentage of steatite, which enables them to withstand sudden changes of pressure and temperature without rupture. In every branch of the industry special wares are made for specific purposes—laboratory porcelain, porous wares of various kinds, architectural faience that will withstand our climatic conditions, etc.

In 1920, the manufacturers of refractory goods established, under the auspices of the Research Board, the British Refractories Research Association. Dr. Mellor was appointed Director of Research, and with Dr. Scott and others he has already done much valuable work, and we can confidently expect a great advancement of our knowledge in this direction during the next few years. Investigations have been made on the various refractory clays found in this country and their chemical and physical properties at high temperatures, standards of composition, and of firing temperature and condition have been established, and the whole industry is gradually being built up on sound scientific lines. The manufacture and use of high-grade silica bricks has greatly increased during the last ten years and many other refractory materials have been brought into commercial use. These include zircon, zirconia, carborundum, sillimanite, corundum, certain bauxitic fireclays, etc. Magnesite has long been used and has received attention, and many new combinations of refractory materials are under investigation.

During the last twenty years a great amount of work has been done in connection with the constitution and properties of pottery glazes and the interaction between the body and glaze during the firing process, and not only have great changes been introduced in the practice of ordinary glaze-making, but many new types of glaze have been brought into use.

The glaze on pottery is a thin coating of glass which is produced during the glost firing by the melting together of certain finely-ground materials which have been applied to the surface of the ware. The simple glazes often used even up to the present time for ordinary earthenware are prepared by mixing together finely-ground white lead and flint with or without the addition of Cornish stone or whiting. These are known as " raw " glazes, but their use is becoming less and less common, and more complex glaze mixtures are now generally used. Boracic acid is a very valuable glaze-making material both because of the fluidity it imparts to a glaze and because of its well-known colour-developing qualities. It also gives the glaze-maker a wider range in the proportions and nature of the bases used. Since glaze is generally applied in suspension in water, it is not practicable to use any soluble raw material in the glaze mixture, so that the soluble ingredients such as borax, soda ash, etc., are first melted together with certain proportions of whiting, sand, or flint, and sometimes Cornish stone, felspar, China clay, etc. This produces a compound borosilicate glass or " frit," as it is called, which is run into water and afterwards ground together with a certain amount of " mill mixing " which may be white-lead, Cornish stone, flint, felspar, China clay, or any other insoluble glaze-making material. In recent years it has become the practice on many works to abandon the use of raw-lead glazes for general purposes and to use instead lead-bisilicate, prepared by fritting together the correct proportions of red lead and sand. This change has been brought about in the interest of the pottery operatives who use or handle lead glazes, for whereas white lead is readily and completely soluble in very dilute hydrochloric acid (and therefore presumably in gastric juice), lead bisilicate is only very slightly soluble, the particles under the action of dilute hydrochloric acid becoming almost immediately coated with a layer of silicic acid which protects the particle from further action.

Lead silicates and borosilicates have extremely valuable glaze-making qualities which are not possessed to the same degree by any other known substances. They mature at a comparatively low heat and remain without deterioration through a wide range of temperature, they do not devitrify under normal conditions of firing, they give fluidity with sufficient viscosity to prevent excessive " running " in the glost fire, and they have certain characteristic colour-developing qualities in conjunction with the colouring oxides and prepared pigments used in pottery decoration. Nevertheless, as a result of the investigations on the action of lead in glazes, a series of leadless glazes has been prepared, and such glaze is now very largely used in certain branches of the industry, especially in the sanitary section. The tendency of leadless glaze to become opaque or opalescent (probably due to devitrification) has also been exploited, and certain leadless glazes are used which become clouded and opalescent during the firing and so produce interesting artistic qualities of colour and glaze. Further, a series of semi-dull or matt glazes is now in common use. These are produced by the addition of whiting, oxide of zinc, oxide of tin, oxide of titanium (rutile), or China clay to the ordinary stained glaze. It seems probable that these materials added in excess remain partly in suspension in the glaze and thus produce a dull surface of fine egg-shell quality. The usual colouring oxides used are those of copper, cobalt, iron, manganese, and chromium, and to a less extent nickel, uranium, and iridium. Certain other mineral substances are also used, such as chromite, whilst oxide of tin and zirconia, and certain fluorides and phosphates, are used to produce opacity. Many new tints and colour effects have been produced in the last few years by the use of glazes of certain new chemical types. The preparation of pottery colours for underglaze and onglaze decoration, the action of glazes of different types on these prepared colours, and also the effect produced

by such glazes on the colour developing properties of the metallic oxides have been closely studied. At the same time, the action of a reducing atmosphere on certain glazes and metallic oxides has been used to produce flambé and lustre effects on a commercial basis. Decorative stoneware of fine quality is being more largely made, and altogether the range of underglaze colours, of coloured glazes and matt glazes, of opalescent, splashed, crystalline, flambé, and other texture glaze effects has been enormously extended since the beginning of this century, and this country holds a pre-eminent position in the production of these so-called " artistic " effects on pottery and tiles. The flambé glazes and lustre effects are of especial interest to the chemist. Oxide of copper added to a glaze will produce under oxidising firing conditions a coloured glaze varying in tint according to the type of glaze, from a grass green with a lead glaze to a turquoise blue with an alkaline glaze (Egyptian turquoise glaze, for example). If, however, a glaze containing as little as 0·5% of oxide of copper is fired in a reducing atmosphere, a strongly stained red-coloured glaze is produced. This colour is so intense considering the small amount of colouring oxide used that it is probably due to the presence of very finely-divided metallic copper, although some of the sub-oxides may be present also. A little tin oxide is often added to the glaze, and it probably acts as an oxygen carrier and helps in the reduction of the copper oxide. The coloured glaze so produced is often " splashed " in effect and is generally known as " rouge flambé." Mr. Moore has also produced many interesting and beautiful glaze effects of this type by the introduction of other metals than copper. The lustre effects are produced in two distinct ways. What is known as " smoke lustre " is a revival of the lustre effects of the Ancient Persian and the mediæval Hispano-Moresque and Italian potters. For this purpose, sulphides or organic salts of silver and copper are finely ground with a proportion of burnt or raw clay and then mixed with a suitable medium and applied to the surface of the already fired glaze. The ware is then refired at a comparatively low temperature—600° to 700° C.—in a reducing atmosphere. It seems probable that under these firing conditions volatile sulphides or organic salts of the metals penetrate the softened surface of the glaze, and are there decomposed by the silicic acid present and thus a thin film of metal is deposited in and on the upper surface of the glaze. This film of metal is so thin that it produces " interference " colours or iridescence. The metal also dissolves to some extent in the glaze, and altogether the effects produced are very subtle but often striking and beautiful, and they have a quality which cannot be obtained in any other way. The other and more modern type of lustre effect is produced under the ordinary oxidising firing conditions. It has been known for some seventy years that certain salts of bismuth, when thinly applied to glazed pottery and fired in the ordinary enamel kiln, would produce a lustrous effect (Belleek lustre, for example), but within recent years a wide range of bismuth lustres has been introduced. The basis of these lustres is a so-called " resinate " or " sulphoresinate " of bismuth which is mixed with lavender oil to enable it to be painted very thinly on the surface of the fired glaze, which is then re-fired in the enamel kiln. Various colours are obtained by addition of salts of other metals.

Perhaps the most important modern development in pottery practice is the extension of the use of the casting method. The process of casting has been in use in this country for nearly two centuries. Prepared clay is mixed with sufficient water to make a clay slip of the consistency of cream. The slip is poured into open porous moulds—generally plaster of Paris—which absorb water and so become coated with the clay that was in suspension in that water. When the deposit of clay is of sufficient thickness the remainder of the slip is poured out, leaving behind a clay vessel that corresponds exactly in form with the inside of the mould. The slip

used for this purpose contains approximately equal parts by weight of clay and water, and if more clay be added the slip becomes too thick for satisfactory working. It was discovered about the beginning of this century that the addition of certain hydrolysable salts rendered clay slip much more fluid, and in practice it is found that the addition of 0·4% of sodium silicate and sodium carbonate together will enable the potter to use a slip containing less than 25% of water—about the same amount as is contained in a soft plastic clay. The use of this dense clay slip has revolutionised the sanitary industry. Cores can be used in the moulds, and large pieces of ware having thick walls can be successfully cast. The prepared slip is pumped into storage tanks, from which it flows through pipes to the potter's bench, where the moulds are filled from taps—a much quicker, simpler, and more economical method than the former one of filling the mould with plastic clay by hand. This new casting process is used in other branches of the industry, and even large pieces of fireclay goods are in some cases so made.

Within quite recent years much more accurate methods of determining the temperature of the ovens at various stages of the firing have been introduced. By means of recording pyrometers the rate of increase of temperature and the corresponding changes produced in the ware can be studied and an ideal firing curve arrived at for every type of ware. The older forms of pyrometer which measure the contraction of test-pieces of clay or body, and fusion cones, are still generally used. The thermoelectric and photometric pyrometers indicate temperature only, whereas the contraction and fusion cone types register the effect of temperature into time—an important advantage. The effective factor in firing is not temperature alone, but temperature into time, and within certain limits the same results are produced by firing for a shorter time at a higher temperature as by firing for a longer time at a lower temperature. Even the re-firing of ware to the same temperature as before will produce further chemical and physical changes, a result to be expected where arrested chemical action is concerned. The best temperature–time equation varies for different types of ware, and the use of recording pyrometers and the study of firing generally, have resulted in the collection of much valuable information in this direction, some of which has been put to practical use. During the last twenty years many new types of ovens for firing pottery have been introduced. These are mainly gas-fired continuous or semi-continuous plants, and the otherwise waste heat of the cooling ware and of the firing gases is largely utilised and considerable saving of fuel thus effected. These continuous ovens are of two main types. One is the Mendheim type and consists of a series of firing chambers joined in circuit. The goods are placed in the chambers and the fire is made to travel very slowly round the circuit, each chamber in turn being fired up by the introduction of producer gas along one side, which is burnt by hot air which has been heated by travelling through three or four of the chambers last fired-up. The hot products of combustion travel forward through several chambers on their way to the chimney flue, and so much heat is withdrawn from these gases that the chamber in advance of the one under gas generally attains a temperature of about 800° C. before any producer gas is introduced. The other type is known as the "tunnel-oven." In this case a constant zone of high temperature is maintained in the middle of a long firebrick tunnel. The goods to be fired are placed on trucks which run on rails through the tunnel at a speed of from three to twelve feet per hour. The tunnels vary in length from 100 to over 300 feet, and the goods are slowly fired up as they pass into and through the firing zone and are then slowly cooled as they pass on to the end. The air for the combustion of the gas is heated by passing over the cooling goods, and the chimney flue or fan extracts the products of combustion near the end at which the goods enter. In this way most

of the otherwise waste heat is utilised. Tunnel ovens are of two types—the open fired, where the combustion of the producer gas takes place in the open tunnel—and the muffle type, where the combustion is confined to insulated combustion chambers and in which the products of combustion do not come in contact with the ware. Many continuous-firing plants are now in operation and they are giving on the whole excellent results. They are smokeless, very economical in fuel consumption, and they produce ware of more standard quality than that produced on the older types of oven and kiln. Several of these types of continuous gas-fired ovens, which have been designed in this country, have been erected on the Continent, in the United States, in Japan, and other countries. Amongst these are the " Donnachie " kiln and the " Shaw " kiln (both of the " Mendheim " chamber type), the " Dressler " tunnel oven (insulated combustion chambers), and the " Marlowe " tunnel oven (open-fired), each named after the original designer.

Other types of oven have been introduced. In some cases a recuperative system has been applied to single firing chambers, and much experimental work is being carried out in connection with the firing of ware of all kinds.

British pottery manufacturers generally are wakening up, and the past few years have shown great advances not only in our knowledge of the many chemical and physical problems with which the potter has to deal, but in the application of this knowledge in many directions, and in the erection of new and more efficient firing plants, and the introduction of machines and mechanical contrivances in many processes which were until recently carried out by hand. There is a decided tendency towards mass production with its standardisation methods which lead to more efficient and cheaper production. On the other hand, this system is apt to crush out the wonderfully capable craftsmen that this country has produced in the past, and to bring about a consequent lowering in general and artistic quality of certain classes of ware.

FLAME, FUEL AND EXPLOSION

By H. F. Coward, D.Sc.

The line of demarcation between scientific research and industrial research in such subjects as fuel is ill-defined, and it is hardly possible to restrict this account of recent British contributions in this subject to the purely scientific side. The interdependence of science and practice is illustrated by the numerous important advances in the more purely scientific knowledge of fuel and flame which technical workers have made in their efforts to provide the fundamental knowledge necessary for industrial progress. Of the bodies which have contributed in this way may be mentioned the Home Office Explosions in Mines Committee, the Safety in Mines Research Board of the Mines Department, the Doncaster Coal Owners' Association, the Fuel Research Board of the Scientific and Industrial Research Department, and the Lancashire and Cheshire Coal Research Association. The Universities of Manchester, Leeds, Sheffield, and Glasgow, and the Imperial College of Science and Technology, may be mentioned for their conspicuous share in recent developments in this branch of science.

Fuel

Three years ago there was formed a "Coal Research Club," which immediately produced a new journal, *Fuel in Science and Practice*. This journal, now in its third year of issue, already embodies a meritorious collection of original papers, abstracts, and reviews.

Sir George Beilby described the Coal Research Club, on its inception, as "a small body of scientific workers who are studying the physical and chemical constitution of coal, in the belief that the knowledge so acquired will have an important bearing on the practical and more economical methods for the utilisation of coal and its products as fuel." That defines the fundamental problem of British fuel, and serves to indicate the main subject discussed in the report below.

Constitution of Coal.—Coal is generally believed to be an assemblage of plant products in various stages of decay; some of these products retain their original organised structure, others are structureless. Such a mass composed of a large number of highly complex chemical individuals presents a difficult problem of analysis, and the difficulty in the case of coal is enhanced by the fact that the substances are in many cases closely related chemically, are not at all readily soluble or dispersible in liquid reagents, and are not crystallisable. A satisfactory analysis must clearly involve a separate examination of the composition and properties of each of the constituent parts, namely, the representatives of the woody tissue, the bark, spores, cuticle, waxes, and resins of the plant, and the structureless products—ulmins—formed during vegetable decay. A detailed discussion of this subject appears in a memoir on "The Constitution of Coal," by Marie C. Stopes and R. V. Wheeler (1918).

The minute knowledge postulated in the previous paragraph as desirable will take long to obtain, but the first steps towards a grosser differentiation of coal constituents have been made with some success. Casual inspection of almost any lump of bituminous coal shows the presence of a series of dull and bright bands. Closer examination has led Marie C. Stopes to distinguish four constituents which can be recognised by the naked eye and which differ in their minute structure as revealed by the microscope. These are (1) Fusain, consisting of powdery fibrous strands which under the microscope are seen to be fibres of woody cells with thickened and blackened walls. (2) Durain, dull, hard coal containing plant remains, in particular

macro- and micro-spores embedded in a matrix of granular particles. (3) Clarain, ordinary bright coal containing the greatest variety of plant remains, such as stem- and leaf-tissue, cuticle, and spores. (4) Vitrain, more brilliant in appearance than clarain, fracture conchoidal, structureless, and uniform texture like that of glass.* These four constituents have, with some trouble, been isolated from a Hamstead coal in quantities sufficient for laboratory experiments, and have been examined chemically by F. V. Tideswell and R. V. Wheeler. They found considerable differences in every property examined—density, chemical composition, moisture and ash content, solubility in the common coal solvents, and behaviour on distillation; for each property the same order was maintained, namely, fusain, durain, clarain, vitrain, with the first-named occasionally exhibiting anomalous behaviour. As regards coking properties, R. Lessing found that when he attempted to coke the powdered constituents separately, fusain showed no change in appearance and no tendency towards cohesion, durain had only slight cohesion, clarain showed considerable fusion and merging of particles, vitrain was well sintered together, but the consolidation of particles was not so complete as with clarain. The ash content varied not only in amount, but also in composition, on passing from one constituent to another.

Constitution of Coal. α-, β-, and γ-Compounds.—Earlier investigations had shown that the substance of coal, as a whole, could be divided by the prolonged action of suitable solvents into the groups of compounds.

α . . .	Insoluble in pyridine.
β . . .	Soluble in pyridine, but insoluble in chloroform.
γ . . .	Soluble in pyridine and also in chloroform.

The α- and β-compounds differ but little from one another except in the physical structure which determines the ease of dispersion in pyridine; the γ-group is very different, as the following comparison shows;

α- and β-Compounds.	γ-Compounds.
(1) Infusible.	Melt at 95–100° C.
(2) Yield but little liquid products on destructive distillation; these are mainly phenolic.	Yield about half their weight of liquid products on destructive distillation; these are mainly "resinic" in character and contain no phenols.
(3) Yield as gases on destructive distillation mainly hydrogen and oxides of carbon.	Yield as gases on destructive distillation mainly the paraffin hydrocarbons.

The α- and β-portions have been identified by Wheeler and his co-workers as representing those portions of the coal derived from cellulosic materials (in a general sense); the γ-portion, on the other hand, is derived from the oils, resins, and waxes of the original plants.

Each of the four constituents of bituminous coal may contain any or all of the three types of compounds, α, β, and γ; but the proportions of these vary. Thus, for example, the non-caking fusain is always relatively poor in γ-compounds, which seem to represent the caking material responsible for the coherence of coke.

* Three of these constituents of bituminous coal have recently been recognised microscopically in anthracite, by C. A. Seyler.

Extraction of coal by pyridine must be conducted in the absence of free oxygen, for W. A. Bone has shown that the amount of extract may be altered if the operation is performed in the presence of air. In addition, it appears that the relative proportions of α-, β-, and γ-compounds can be altered by prolonged heating at low temperatures, and S. R. Illingworth has recently made propositions based on this to modify the coking properties of coal by pre-heating it at suitable low temperatures.

The Combustion of Coal.—The first stages in the oxidation of coal have been investigated with some success, for R. V. Wheeler has shown that oxygen forms an additive compound with one or more of the substances present in coal—which of these remains to be discovered. It has been shown, however, that the facility for oxidation of coal runs parallel with the amount of oxygen already in combination in the coal itself; thus the temperature of rapid self-heating of a powdered coal loosely packed in a tube through which a current of air was passed ran from 165° to 220° as the percentage of oxygen in the coal fell from 11·1 to 3·9. Later work, in collaboration with F. V. Tideswell, has shown that vitrain and clarain are more liable to oxidise and ignite than durain. The influence of fusain is variable, for while a sample from the Hamstead coal was very readily oxidisable, other samples examined by J. I. Graham showed the reverse. Fusain may, however, be a contributory cause of spontaneous combustion of coal, not by its own oxidation, but by reason of its porous nature, which may afford an easy access of oxygen to the bright portions of the coal with which it is frequently associated.

The explosive inflammation of coal dust is a subject treated in some detail in connection with the exhibit of the Safety in Mines Research Board of the Mines Department, but one of the earliest experiments on the subject is represented by the exhibit, by P. P. Bedson, of an apparatus with which he succeeded many years ago in determining the sensitiveness to explosive inflammation of coal dusts from various sources, the influence of composition, the effect of inert materials and of the physical condition of the dust, and, finally, the mechanical effects of the explosions. The same exhibitor first discovered the solvent effect of pyridine on part of the coal substance, and proved in this apparatus the superior explosibility of the extractable material over that of the rest of the coal.

Air Pollution and Smoke Prevention.—Apparatus for recording continuously the relative amount of pollution of the air by coal smoke has been made successfully by W. Thomson and by J. Owens, and records obtained by this means show the variation in air pollution from hour to hour, in chosen places, and show the influence of atmospheric conditions. It is now generally agreed that industrial operations are by no means the only important source of pollution, but that domestic fires alone are sufficient to cause highly objectionable and costly pollution.

No simple cure appears possible; but much scientific work lies at the foundation of the improvements, already visible in the big cities, which have been effected by improved industrial stoking and by the partial substitution of open coal fires by gas fires, electric stoves, radiators, and so forth. The Manchester Air Pollution Committee have published an account of Margaret Fishenden's measurements of the amount of radiation from open fires of different kinds burning coals and smokeless fuels of the " coalite" type; and the radiation from gas fires has been carefully examined by W. A. Bone and others for the Institution of Gas Engineers, thus providing data to assist the design of gas fires.

The coal fire, however, remains. The provision of a smokeless " coalite " which shall be acceptable to the housewife on all grounds, including that of price, seems to be the outstanding

problem; and everyone resident in a large city must have been convinced during the coal strike of 1921 of the immense advantage of a satisfactory solution to the problem of cleansing the air from coal smoke pollution.

Smoke is objectionable not only on account of its dirtiness, but because it represents lost energy. Apart, however, from visible smoke, some hundredths of a per cent. of carbon monoxide, methane and unsaturated hydrocarbons are present in the flue gases from domestic fires, as F. S. Sinnatt has recently found by using special methods of gas analysis. These invisible impurities represent a loss of some 10 % of the coal used for domestic purposes, *i.e.* a loss of some 4,000,000 tons of coal annually.

The Distillation of Coal.—Most of the fundamental investigations on this subject carried out in recent years have aimed at obtaining information which should elucidate the nature of the coal substance itself, and as such have already received brief mention.

The gaseous products of the distillation of coal in a vacuum at low temperatures have been examined in detail by M. J. Burgess and R. V. Wheeler, who proved the presence of each of the paraffin hydrocarbons up to pentane, ethylene and higher olefines, hydrogen, carbon dioxide, carbon monoxide, and hydrogen sulphide, but were unable to detect any benzene vapour among the low temperature distillation products.

The sulphur compounds which invariably occur intimately associated with coal give rise to sulphur compounds in the gaseous products of distillation. The sulphur compounds recognised in coal gas are sulphuretted hydrogen, present in large quantities, carbon bisulphide, present in much smaller amount, and thiophene and others present in minute traces. On combustion of such gas the oxidation of the sulphur compounds gives rise to sulphur dioxide and ultimately sulphuric acid in such amounts as to render impossible the use of unpurified coal gas in the atmosphere of an inhabited room. The complete removal of sulphuretted hydrogen has long been accomplished by the use of lime, or, better, of hydrated ferric oxide, but it is only during the present generation that the removal of carbon bisulphide has become a commercial success, by a process devised by E. V. Evans and developed in collaboration with C. Carpenter at the South Metropolitan Gas Works. Their technical scientific skill has now removed this constituent of gas, which was responsible for much corroding of brass fittings and destruction of leather.

The nitrogenous constituents of coal give rise to ammonia on distillation, and thus provide what was until recently the chief means for artificial enrichment of soil in combined nitrogen. J. W. Cobb and his colleagues have much enlarged our knowledge of the possibilities of obtaining an increased conversion of the nitrogen of coal into ammonia, by variations in the conditions of distillation.

The thermal phenomena accompanying the carbonisation of coal are complex, and Cobb has found that as the temperature of coal is raised, a succession of exothermic and endothermic reactions is observed.

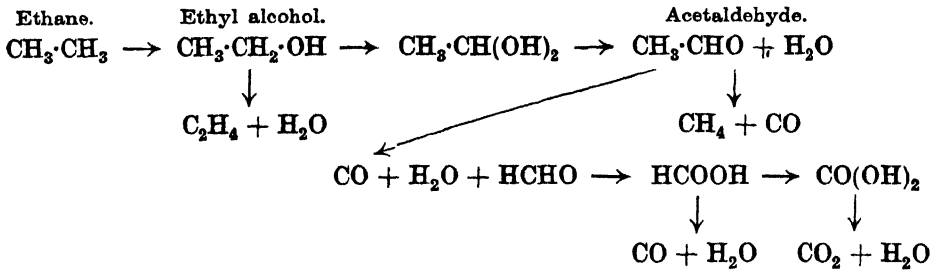
Flame

The experimental study of flame during the past twenty years has been pursued nowhere with more success than in Britain. The foundations lie in the discoveries of a succession of eminent experimentalists, made during the last century; in Humphry Davy's investigations on the ignition of gases, on surface combustion, and on the propagation and extinction of flame,

one result of which was the invention of the miner's safety lamp; John Dalton's discovery of the nature of the products of incomplete combustion of methane and ethylene; Michael Faraday's investigation and theory of surface combustion; Edward Frankland's experiments on the source of luminosity of coal-gas flames; H. B. Dixon's discovery that dry carbon monoxide will not inflame in dry oxygen, and its fruitful consequences in Brereton Baker's discovery of the necessity for moisture in many cases, not only of combustion, but also of chemical reaction in general; then also, contemporaneously with distinguished Frenchmen, Dixon's investigations on the detonation of explosive gas mixtures; and, finally, A. Smithells' separation of the two cones of a non-luminous coal-gas flame.

The Manchester laboratories, directed until recently by H. B. Dixon, have produced a succession of investigations on the subject of flame, and investigators who have obtained their initiation into the technique of flame research there have proceeded to the successful reduction of the dangers of explosions in collieries, and to industrial invention in the domain of gas fires and various types of commercial heating apparatus. Another school of work on flame has been stimulated by the engineering problems of the internal combustion motor, led by Bertram Hopkinson at Cambridge and by Dugald Clerk.

The Chemical Reactions of Hydrocarbon Combustion received detailed study during the first decade of the present century by W. A. Bone and his collaborators, who disproved the simple current theories of hydrocarbon combustion, and concluded from their experiments that oxygen becomes incorporated into the hydrocarbon molecule step by step to produce a series of hydroxylated molecules, each of which may undergo thermal decomposition or further oxidation, according to circumstances. Thus, for example, the oxidation of ethane is represented now by the succession of products:



Of the various modes of oxidation and decomposition indicated, the predominance of one or another depends on the relative amounts of hydrocarbon and oxygen, and on the temperature attained.

The Ignition Temperatures of Inflammable Substances.—For long it has been thought that the ignition temperature of an inflammable substance may be as characteristic of that substance as its melting point or boiling point. The latter properties are functions of the pressure, and ignition temperatures are similarly dependent on experimental conditions. Of these latter, the influence of solid surfaces in contact with the gases under observation is a factor wayward in nature and incalculable. H. B. Dixon's efforts have been directed to the elimination of surface action, with apparent success, in two independent methods of experiment. In the first, a determination is made of the temperature necessary to pre-heat the combustible gas and the supporter of combustion separately, so that inflammation occurs on admixture

and the observation recorded is therefore the temperature at which rapid self-heating occurs when the one gas issues into an atmosphere at the same temperature. In the other experimental method, advantage is taken of the heat developed by the work done on sudden compression of an explosive mixture of gases to cause inflammation. The temperature attained has been calculated on the assumption that the sudden compression of gas has been accomplished adiabatically. Lately, this assumption has been examined experimentally by H. T. Tizard, and he has obtained indicator diagrams of the compression under conditions which he prefers to term sudden, not adiabatic; the resulting calculation gives a lower figure for the ignition temperature than Dixon's.

The following results are selected for illustration:

Ignition Temperature of a jet of pre-heated gas flowing into an atmosphere of equal temperature is, at atmospheric pressure:

	In oxygen.	In air.
Hydrogen	585° C.	585° C.
Carbon monoxide	650	650
Acetylene	430	430
Hydrogen sulphide	227	364
Methane	556–700	650–750

Ignition temperatures, determined by the method of "adiabatic" compression, at the pressure producing ignition, are for

$10H_2 + O_2$	676° C.	$2H_2 + \overbrace{O_2 + 4N_2}^{\text{Air}}$	571° C.
$2H_2 + O_2$	526		
$H_2 + 8O_2$	472		

Ignition temperature obtained by the method of "sudden" compression, with the aid of an indicator diagram, for a mixture of approximate composition $2H_2 + O_2 + 4N_2$, is 407° C.

The methane ignition temperatures quoted above extend over a considerable range; this observation may be related to the variability (with composition) of the ignition temperature of static mixtures of methane and air in contact with a hot surface; and may prove to have an intimate connection with the prolonged "lag" in ignition characteristic of methane, so marked that it is possible to keep methane–air mixtures of appropriate composition in a small vessel maintained at 700° C. for a period of ten seconds, at the end of which inflammation of the mass suddenly occurs.

The relative ignition temperatures of a series of liquid fuels available for use in petrol and in Diesel engines have been determined by Harold Moore in an apparatus which pre-heats the oxygen supply to the temperature at which a drop of the fuel is evaporated; the results have been used in the discussion of the problem of avoidance of "knocking" in these engines.

Ignition by Electric Sparks.—The ignition of gaseous mixtures by the electric spark is repeated hundreds or thousands of times during each minute by every internal combustion engine, except by those of the Diesel type; yet this phenomenon has received very slight scientific

analysis. It is easy to produce, by a spark, flames in diluted mixtures which are incapable of propagation for more than a few centimetres; it is less easy to ignite a strongly explosive mixture such as electrolytic gas when the pressure is low, but sufficiently powerful sparks may produce self-propagating flame in this mixture at pressures no greater than 8 mm. of mercury, and the sensitiveness to ignition of series of gas mixtures has been compared by the measurement of their limiting ignition pressures for a constant sparking arrangement. Further advance has, however, been made quite recently as a result of physical studies of the spark, and it appears that in certain instances ignition is due to the capacity component of the spark, the inductance component contributing nothing.

Limits of Inflammability of Gaseous Mixtures.—It is almost self-evident that a minimum amount of combustible gas must be present to form an inflammable mixture with air (or other supporter of combustion), and, on the other hand, that there is an upper limit to the amount of combustible gas which may be present if the mixture is to remain inflammable. The present writer and his colleagues have shown that the limiting composition of mixtures which are capable of indefinite propagation of flame, when maintained at atmopheric presssure and temperature ahead of the advancing flame, are :

Hydrogen	4·1 to 74·2% in air.
Methane	5·6 to 15·4 ,,
Carbon monoxide	12·5 to 74·2 ,,

The experiments which established these figures required the use of exceptionally large vessels, 15 feet long in one case, 1 foot square in another, and brought to light some unexpected phenomena. For example, hydrogen–air and coal-gas–air mixtures, somewhat above the lower limit, exhibited on ignition vortex rings of flame which rose for some distance and then broke up into small balls of flame capable of travelling apparently indefinitely up through the mixtures. This observation served to elucidate certain curious phenomena noted occasionally in confined spaces in which electric storage cells, being charged, are liberating hydrogen gas.

It has also been proved that all mixtures of limit mixtures (provided they be of one type, that is, either lower limit or upper limit mixtures) are themselves limit mixtures; from which generalisation may be calculated the two limits of any complex mixture of inflammable gases, such as coal-gas.

When it is a question of determining the influence of relatively great variations of temperature and pressure on the limits of inflammability, or when the gases under examination are not available in large quantity, the procedure described becomes impracticable. In these circumstances, experiments which give the relative limits of inflammability within a smaller vessel, for upward, downward, or horizontal propagation as desired, serve to elucidate the influence of the various factors named. From a series of publications by R. V. Wheeler and colleagues it appears that the methane–air limits are considerably widened by increase of temperature; the pressure effect is curious, in that the limits are narrowed by decrease of pressure below the normal, and above atmospheric are widened on the upper limit side, but narrowed on the lower limit side. This last observation finds its parallel in the case of each paraffin hydrocarbon from ethane to pentane, but the point of inflexion of the lower limit curve occurs at higher pressures as the molecular weight of the inflammable gas increases.

A surprising result arose from experiments in which turbulence was induced in the gases by

the rotation of a fan; mixtures of methane and air containing rather less methane than was necessary to propagate flame when at rest exploded violently when the fan was revolving.

Propagation of Flame in Non-detonating Mixtures.—The most extensive research in recent years on the propagation of flame in mixtures which do not detonate has been carried out by R. V. Wheeler and his colleagues, especially by W. Payman, on the behaviour of various methane–air mixtures ranging in composition between the limits of inflammability. These mixtures propagate flame so slowly when their composition approaches the limits of inflammability that the passage of the flame can readily be followed by the eye. The precise rate of propagation depends on the diameter of the tube containing the mixture, and propagation is, as has long been known, impossible in sufficiently narrow tubes. As the methane content increases above the lower limit amount, or decreases below the upper limit amount, the rate of propagation of flame increases until at a composition of 10% methane with 90% air, the flame has its greatest speed. The composition of the maximum-speed mixture is the same whatever the manner of propagation of flame (apart from detonation, which has never been induced in any methane–air mixture), for example, whether flame travels along a horizontal or a vertical tube, or whether it travels from an open end to the closed end of a tube, or *vice versâ*. While, however, the maximum falls at this constant composition figure, the actual speeds vary considerably according to the direction of the flame, so that a flame travelling from the closed end of a tube may travel twenty or more times faster than a flame moving in the same mixture but in the opposite direction.

Photographs of the passage of flame in methane–air mixtures have become possible with the aid of quartz apparatus.

A new generalisation relating to the speed of uniform movement of flame has recently been put forth and well tested by W. Payman, to the effect that when mixtures of gases of equal flame speed are mixed, the resultant mixture has the same speed of flame. An unexpected development from this has been a criticism of conclusions, drawn by W. A. Bone from certain explosion experiments, concerning the relative affinities of methane and hydrogen for oxygen.

Detonation.—The term originally applied to the flame of high and constant speed which develops in many explosive gas mixtures after the preliminary periods of uniform propagation and of vibratory movement, a flame which may attain a speed of 3,500 metres per second, was that of the detonation wave. The theoretical and experimental investigation of this phenomenon in Britain has been confined to the Manchester School, who have discovered the retonation wave which travels back through the still burning gas from the point when detonation starts, the effects of collision between two explosion waves, and of the passage of reflected waves through the hot products of combustion. In recent years, the term has been applied, or perhaps misapplied would be a better description in the present state of knowledge, to the " knocking " of internal combustion engines. On this latter point we have some illuminating experiments by H. R. Ricardo which show the intimate connection between the compression ratio of the engine cylinder and the nature of the fuel used, according as it is composed of paraffin, hydroaromatic, or benzenoid hydrocarbons; and H. T. Tizard has deduced a connection between " knocking " and the ignition temperatures and temperature coefficients of rate of oxidation of hydrogen and hydrocarbon fuels.

Turbulence and the Speed of Flame.—The technical importance of turbulence was first pointed out by Dugald Clerk, who stated, in 1913, that he had long ago observed that gas engines would have been impracticable had the rates of explosion been the same in actual engine

cylinders as in closed-vessel experiments. He demonstrated with a gas engine that the maximum pressure on explosion was attained two or three times more rapidly in a normal stroke than was the case when ignition was produced at the end of the third compression stroke, after the charge had been expanded and compressed twice without firing, when turbulence had more or less subsided. Bertram Hopkinson confirmed this observation independently by firing mixtures in which turbulence was induced by a fan, and in one case reduced the time of attainment of maximum pressure from 0·13 second in a mixture at rest to 0·02 second in a mixture rendered turbulent by a fan running at 4,500 revolutions per minute. R. V. Wheeler has examined this phenomenon in detail with mixtures of ethane and air in various proportions, measuring the speed of flame in turbulent and non-turbulent mixtures, and finding that the ratio between the two speeds runs from about 4·0 in the slow burning mixtures to 2·4 in those which burn most rapidly. In both cases the time of maximum pressure coincides with the complete inflammation of the mixture.

Pressure Produced by Gaseous Explosions.—Internal combustion engine research has been concerned with the specific heat of gases, the heat radiated from flames and conducted to the cylinder walls, and to the completeness of the reactions of combustion at the moment of maximum pressure. Reference should be made to a series of Reports of the British Association Committee on Gaseous Explosions for an adequate summary of this involved problem, but one or two of the scientific aspects may be mentioned here. First, it appears that a heat loss of the order of 5 to 20% is to be attributed to radiation from flames; that this is due to radiation from the hot products of combustion, of which carbon dioxide is about two and half times as radiant as steam; and that the radiations from carbon dioxide and steam respectively are characterised by definite wave-lengths. Secondly, there still appears to be some doubt as to whether there is coincidence between the times of complete travel of flame through a cylinder and of maximum pressure development.

Quite recently an interesting conclusion has been drawn by W. A. Bone' from a study of pressure curves obtained in explosion of mixtures of carbon monoxide and oxygen with various diluents, under high initial pressure. It seems that in these circumstances a notable amount of energy is absorbed by nitrogen, not exhibited as thermal energy, in contradistinction to other gases. Speculations arise as to the manner in which the nitrogen molecule disposes of this energy, and apparently the natural conclusion that this occurs by formation of nitric oxide is excluded.

Surface Combustion.—The interaction of hydrogen and oxygen at temperatures below their ignition temperature on the surfaces of various materials received detailed study in the early years of the present century by W. A. Bone and R. V. Wheeler. The theoretical results of this, so far as concerns the precise nature of the catalytic behaviour of a surface, may be roughly described as the qualitative adumbration of the quantitative results which Langmuir has obtained in connection with the surface film in heterogeneous catalysis. The practical result was the successful construction of surface combustion heaters for industrial use.

EXPLOSIVES

By Sir Robert Robertson, K.B.E., F.R.S.

A description of the progress of the British Explosives Industry since the beginning of this century can conveniently be divided into three sections:

I. The position in 1900.
II. Progress from 1900 to 1914.
III. Progress from 1914 to the present time.

I. **The Position in 1900.**—The first practical smokeless propellant powder made on the principle of partially gelatinising nitrocellulose by a solvent was the E.C. sporting powder brought out in 1882 by Mr. Walter F. Reid, and this exemplifies a type of sporting powder still manufactured.

Alfred Nobel's discovery in 1887 of the gelatinisation of soluble nitrocellulose by nitroglycerine had led to the manufacture of blasting gelatine and gelignite, and of ballistite for sporting or military purposes, in all of which gelatinisation was brought about by heating. The process of wet-mixing due to Lundholm and Sayers had provided a safe process of mixing the two explosive ingredients for ballistite making.

The military propellant Cordite Mk. I (nitroglycerine 58 %, guncotton 37 %, and mineral jelly 5 %) had been in use for eight years and was manufactured at the Royal Gunpowder Factory and by private firms. The acetone used for gelatinising the guncotton in its manufacture was not recovered; guncotton was made by the Abel pot process and nitroglycerine by methods introduced from the Continent. Gunpowder was still used as a propellant in some large guns, and for the bursting charges of the largest shell, although for certain shells picric acid (lyddite) was the bursting charge, actuated by a rapidly burning mixture of ammonium picrate and potassium nitrate. Wet guncotton was the bursting charge for torpedoes.

At the beginning of this period, research on explosives was reawakening after a considerable pause since the time when Abel and Noble had been actively engaged on the chemistry and effects of explosion of gunpowder and of guncotton, and Brown had discovered that a primer of dry guncotton fired by a fulminate detonator would detonate a charge of wet guncotton.

Action had been taken with regard to the dangers arising from explosion in fiery mines in 1896; after this time, only those explosives which had passed in a testing gallery at Woolwich were permitted to be used in such mines. Equivalence of charge was secured by comparison of the effects of explosion in a Trauzl block.

To the Home Office Inspectors of Explosives power was given under the Explosives Act of 875 to inspect trade factories and magazines. A marked fall in casualties occurred, and the results of their experience have proved of benefit to the industry.

II. **Progress from 1900 to 1914.**—*Manufacture.*—The principal advances in processes of manufacture were made during this period at the Royal Gunpowder Factory, which, under the superintendence of Sir Frederic Nathan, became a model of efficient organisation, safe manufacture, and improved technique.

In the manufacture of guncotton the process of J. M. and W. T. Thomson, in which the waste acids from nitration were displaced by means of water, effected a great improvement on the pot process, in safety, freedom from fumes, completeness of nitration, and economy in labour; eventually it became universally used in this and several other countries. An investigation into the chemistry of the process of stabilising guncotton by Robertson showed the

need for an acid-boiling to break up sulphuric acid esters, and led to greater stability in the product.

The displacement principle in another form was applied by Nathan, Thomson, and Rintoul to the manufacture of nitroglycerine by introducing waste acids from a previous charge at the bottom of the nitrating vessel and so causing the separated nitroglycerine to overflow into the washing tank. By working in this way they secured the advantages of increased safety through the abolition of earthenware cocks, reduction in number and elevation of buildings, and in cost of production, and an increase in the yield from 214 to 230 %. In connection with this process, work on the chemical equilibrium between nitroglycerine and the nitrating acids was done by Rintoul.

As the result of the work of Sir Frederic Nathan, the composition of cordite was altered to 30 % nitroglycerine, 65 % guncotton, and 5 % mineral jelly. This propellant (cordite M.D.) was less erosive to the gun, as it had less nitroglycerine and consequently a lower heat value. The acetone used as a solvent, which hitherto had escaped during the drying of the cordite, was recovered by the bisulphite process and the plant of Robertson and Rintoul. Cordite (M.D. or Mk. I.) was the Service propellant for all guns before the War.

Cordite has also been used to a large extent for various sporting rifles brought out from time to time by the British gun trade, though, in some cases, further modifications of M.D. Cordite, involving principally the introduction of a proportion of metallic salts, have been produced by the principal explosives manufacturers: to this class belong the powders Axite and Moddite.

In shot-gun cartridges, the British powders employed may be divided into three classes: partially gelatinised bulk powders, gelatinised bulk powders, and gelatinised dense powders.

E.C. Powder may be taken as typical of the fibrous bulk powder of the first type. The gelatinised bulk-powder class is represented by Smokeless Diamond, which has been improved in manufacture to secure better ignition and more complete burning by the production of a less dense grain. The British gelatinised dense-powder class is now represented solely by the nitroglycerine powder, Sporting Ballistite, which has also recently been improved in manufacture, Shot-gun Rifleite and Condensed Neonite powders containing no nitroglycerine having disappeared.

Trinitrotoluene was being introduced into the Service as a high explosive just before the War, and tetryl (trinitrophenylmethylnitramine) had been transferred from the experimental scale at Woolwich to that of manufacture at Waltham Abbey.

During this period the principal modifications of blasting explosives were connected with the development of safety explosives for fiery mines. The ballistic pendulum was substituted for the Trauzl blocks for determining the equivalent charges to be fired in the gallery, but suspicion began to be aroused as to the pretensions to safety of the current permitted explosives. At Altofts colliery, near Normanton, a large gallery was erected in which coal-dust explosions of considerable magnitude, initiated by a charge of explosive, and the extinguishing effect of stone dust, were demonstrated for educative purposes, and the physical characteristics of coal-dust explosions were investigated.

A gallery test of greater severity was accordingly adopted in 1913 by the Home Office, in which provision was made for testing safety towards coal dust as well as coal gas. In order to produce explosives which would satisfy this test, considerable proportions of a suitable cooling ingredient, usually sodium chloride, were introduced into the existing permitted explosives, with the result that the new explosives were weaker than the old and were more or less powdery, with relatively low density. Gelatinous nitroglycerine explosives of high density containing

cooling agents were added to the list later. The whole position is now being reconsidered by a Committee of the Safety in Mines Research Board under the Chairmanship of Sir Frederic Nathan.

The Committee is engaged in carrying out fundamental research on (*a*) the characteristics of an explosive which determines its liability to ignite mixtures of inflammable gas and air, or coal dust and air, and (*b*) the characteristics and conditions of existence of these inflammable mixtures which enable them to be ignited.

The Committee is also investigating the influence, on the sensitiveness of the gallery tests referred to above, of such factors as the nature and amount of the inflammable gas and of the coal dust used, variations in the method of loading and firing the cannon, and the nature and construction of the gallery itself. The objects in view are to improve the types of coal-mining explosives and the methods of testing them, and by so doing to decrease further accidents in coal mines due to the ignition of fire-damp and coal dust by their use.

Research.—Research on explosives in this period was carried out for the most part at the Royal Gunpowder Factory, at the Research Department, Woolwich, and in the latter half of this period at Nobel's Ardeer factory. Much of this is of a confidential nature, and so reference can be made only to matter which has been published, or to substances which are described as having been adopted into the Service. At Woolwich, from the inception of the Department in 1900 till the present time, explosives research has been successively under the direction of Silberrad (1902–1906), R. Robertson (1907–1921), and G. Rotter (1921), with R. C. Farmer as principal assistant, and at Nobel's under the management of W. Rintoul.

Will had proved that the rate of decomposition of thoroughly purified nitrocelluloses at any given temperature was constant for any particular degree of nitration. By the application of the spectroscope to the gaseous products of decomposition of guncotton (Robertson and Napper), and later to those from nitroglycerine (Robertson), the evolution of nitric peroxide was quantitatively followed; this had an important bearing on the theory of the decomposition of cordite and the stabilising property of mineral jelly, and afforded data for calculating the rate of disengagement of oxides of nitrogen occurring in heat tests (Robertson and Smart).

The constitution of nitrogen iodide was investigated in 1905 by Silberrad, who in 1906, along with Farmer, identified the products of the hydrolytic break-down of nitrocellulose and of nitroglycerine. They also investigated the abnormal character of the hydrolysis of nitrocellulose, and determined the rates of hydrolysis of these two esters, applying the results to the question of storage of propellants under damp conditions.

Later, Farmer returned to the subject of the modes of decomposition of nitrocellulose, distinguishing them as non-catalytic, catalytic, and hydrolytic. He showed that by the choice of an alkali of suitable strength the rate of hydrolysis (or aminolysis) of the ester could be reduced to a minimum, a result which has an important bearing on the action of stabilisers.

The vapour pressure of nitroglycerine at different temperatures was investigated by Marshall, and a method for estimating that explosive put forward by Silberrad, Phillips, and Merriman.

A study of viscosity in connection with the association of certain liquids used as solvents and their action on nitrocellulose was made by Baker in Nobel's Research Department; this subject was destined later to assume great importance.

The calorimetry of propellants began to receive attention, the heat values and gases evolved being determined for Service propellants by Robertson, and for the principal shot-gun propellants by Macnab and Leighton; Macnab and Ristori also estimated the relative temperatures

of explosion by using thermocouples of diminishing thickness exposed to the flame of the explosion. The recording manometer of Petavel for use in determining the pressure set up in a closed vessel when a propellant is fired has proved of great value for this and similar purposes.

Explosives derived from aromatic hydrocarbons began to be studied. Thus a safe method of nitration of dimethylaniline to form tetryl was worked out at Woolwich, and this body was subsequently largely used in ammunition. No trinitrotoluene was made by Government, but it was being experimentally applied and the criteria of its purity were being investigated, a subject on which Rintoul made a communication. The properties of the picrates were investigated by Silberrad and Phillips.

The difficulty of introducing four nitro-groups into the benzene nucleus was overcome by Flürscheim, who prepared the powerful explosive tetranitroaniline.

An estimate of the stability of nitro-aromatic bodies can be obtained by the apparatus and method worked out by Farmer, who heated the explosive in a vacuum and measured by a manometer the rise in pressure due to gases given off by the decomposition. This method has proved of great value, and was applied to the control of the manufacture of tetryl, to the elucidation of the fact that its accelerated decomposition was due to the formation of picric acid (confirmed by Hinshelwood), and to the examination of mercury fulminate.

III. **Progress from 1914 to the Present Time.**—The Great War gave an enormous stimulus, not only to the production of explosives, but also to the study of their properties. New explosives were introduced, new processes of manufacture were started and developed, and innumerable novel requirements arose necessitating the use of explosives. This involved an intensive study of explosives from every point of view, for which the staffs available at the beginning of the War were extremely limited; later, when the policy of withdrawing chemists from the Forces for the purpose of research and manning the explosive factories was adopted, a large body of chemists was initiated into work on explosives and factory management. Thus the section of the Research Department, Woolwich, which dealt with explosives had originally only thirteen chemists, and although these had been trained in the technique of explosive work, the call on them was severe when they were faced with such problems as bringing out a new process for making trinitrotoluene, devising a new propellant, and obtaining a new high explosive for shell, together with devices for detonating it. Finally, there were over one hundred chemists in this Department, which provided advice on explosive matters to the three Services, the Ordnance Committee, and the Department of Explosives Supply presided over by Lord Moulton. As manufacture developed, further assistance both in research and in production was obtained in this country from eminent scientific men, such as Professors Hewitt, Pope, and Lowry, and from representatives of the Dominions, such as Messrs. Burnham from India, Leighton from Australia, and Quinan from South Africa.

Manufacture.—It may give an idea of the enormous expansion of the manufacture of explosives to quote the weekly production at one period of the War: 2,000 tons of cordite, 1,500 tons of trinitrotoluene, 3,000 tons of ammonium nitrate, and 300 tons of picric acid. To produce these were required such weekly quantities as the following: 6,600 tons of pyrites or 2,700 tons of sulphur, 8,300 tons of Chile saltpetre, 720 tons of toluene (from 600,000 tons of coal), 162 tons of phenol (which would have required 1,000,000 tons of coal had synthetic production not been established), 700 tons of ammonia (from 250,000 tons of coal), 374 tons of glycerine (from 2,700 tons of fat), 700 tons of cotton cellulose (from 1060 tons of wastes) and 1200 tons of alcohol and ether (from 4,200 tons of grain). In addition to the above, Canada supplied some trinitro-

toluene, cordite, and nitrocellulose powder, and the United States these explosives and a quantity of picric acid. The demand for acids in the United Kingdom for the manufacture of explosives led to the erection of great plants for making sulphuric acid by the contact process, and nitric acid from Chile nitrate, about 200,000 tons of each being made for this purpose in 1917.

No alteration was made in the methods of manufacture of nitroglycerine and nitrocellulose, the improved processes already described being adopted.

The propellant used by the Navy throughout the War was cordite M.D., for the manufacture of which Sir Frederic Nathan and W. T. Thomson designed a new factory, the Royal Naval Cordite Factory, where were applied all the results of specialised experience in the manufacture of propellants.

It was early found, however, that the demands of the Land Service for propellant could not be met by cordite M.D., in which acetone was used, on account of the shortage of this solvent, notwithstanding the fact that it was produced from carbide at Shawinigan, from alcohol at Warrington, and by fermentation at the Royal Naval Cordite Factory (30 tons a week), at Toronto and at Teere Haute in Canada; the bulk of the supply of acetone, however, came from the United States, which also supplied cordite, as did Canada and, to some extent, the Indian factory.

A new composition (Cordite R.D.B.: nitroglycerine 42 %, soluble nitrocellulose 52 %, mineral jelly 6 %) was worked out at the Research Department by Craig, Robertson, and Rotter, in which guncotton was replaced by a soluble nitrocellulose and the proportion of nitroglycerine altered; ether-alcohol, which could be produced in this country, was used as a solvent. For manufacturing this powder the same machinery could be employed, and no alteration was needed in the gun, as it was designed to have the same heat energy as cordite M.D. This propellant was made at the enormous factory of Gretna, erected by K. B. Quinan, and ultimately at all propellant factories (250,000 tons) except the Naval one. Some new features were introduced into propellant manufacture at the Gretna factory, such as Quinan's method of drying nitrocellulose, which required no mounded buildings.

The alternative to making cordite R.D.B. would have been to import even more of the expensive nitrocellulose powder from the United States. The manufacture of cordite R.D.B. introduced some new problems, principally connected with the purification of cotton from ligneous matter, and the effect of variations in the viscosity of the cellulose on the behaviour of soluble nitrocellulose during the manufacture of cordite. A method for determining the viscosity of cellulose was worked out at the Research Department, Woolwich, by Gibson, and its application to the supply of all the cotton for nitration was organised by the Director of Propellant Supply, Sir Frederic Nathan, and Messrs. Tainsh and Punter of that Department. By ensuring that the cellulose was constant in character, nitrocellulose was produced with a uniformity that enabled the manufacture of R.D.B. cordite to be carried out successfully, so that a product giving the required ballistics was issued from factories in which the labour had been almost entirely unused to this kind of manufacture. The alcohol was for the most part made in this country in distilleries (180,000 tons), although some was imported from the West Indies and Natal. A very large and successful plant for making ether was erected at Gretna. The recovery of the ether-alcohol used as a solvent was effected by means of cresol, a French process, but the scientific principles underlying solvent recovery generally were elucidated at Woolwich in an important study by Masson and McEwan.

In Great Britain nitrocellulose powders were not used for military purposes, or even for the

loading of cartridges for rifled small arms. During the War, however, the manufacture of nitrocellulose powders both for Ordnance purposes and for the service ·303 Mk. VII Cartridge was begun at H.M. Factory, Irvine, where nitrocellulose powder in tubular and multitubular forms was made for field guns and for various howitzers; the powder used for rifle cartridges was in short, tubular grains, whose surface was treated with the object of securing progressive burning.

Since 1918 the use of nitrocellulose powders for various purposes has been considerably developed by the explosives industry. Thus, revolver and rim-fire cartridges are now loaded in some cases with a special nitrocellulose powder produced in very fine flake form. The match-rifle cartridges used at Bisley since 1919 have been loaded with a tubular nitrocellulose powder without any surface moderation.

Before the War, the supply of trinitrotoluene in the country was small and the methods of manufacture were unsatisfactory. One of the first tasks of the Research Department, Woolwich, was to devise a new process, which was evolved as a result of a systematic series of laboratory experiments, followed by demonstration in a small plant on the quarter-ton scale (Craig, Robertson, Farmer, Rotter). The process embodied several novel features, including a regulated temperature rise during the trinitration, the recovery of nitrotoluenes from the waste acids, and a cyclic method of nitration by stages which conserved the strength of the sulphuric in the nitrating acid for the final stage, when it is most required. The process was started at Oldbury about the middle of 1915 in a factory erected by K. B. Quinan, who with the experience gained there put up at Queen's Ferry, near Chester, a trinitrotoluene factory for 700 tons a week. This factory, embodying new principles and new applications, was one of the great technical achievements of the War. At Oldbury, a continuous process for the manufacture of trinitrotoluene from the mononitrotoluene stage was evolved by Holley and Mott. Mononitrotoluene was largely obtained for this factory and also for Queen's Ferry by nitrating a fraction of the Asiatic Petroleum Company's Borneo petroleum, which fortunately contained toluene besides paraffin hydrocarbons. Moreover, a large extension of the country's toluene production from gas works was effected. For many Service purposes, the crude trinitrotoluene after it had been washed free from acids sufficed, but for others symmetrical trinitrotoluene had to be freed from the other isomerides by means of alcohol, for which Hodgkinson developed a process, or by sodium sulphite solution, a French method. In addition to the home production of trinitrotoluene, some was imported from Canada and the United States.

The very urgent need for conserving our supplies of materials for making explosives was urged by Lord Moulton early in the War. To augment the supply of high explosives, Craig, Robertson, and Deacon, of the Research Department, Woolwich, put forward a composition, amatol, together with certain methods of filling it into shell and detonating it. The production of this high explosive, consisting of ammonium nitrate and trinitrotoluene, assumed the proportions of a great industry in which were employed a large number of chemists, including Prof. T. M. Lowry and his staff, who were engaged in improving its manufacture and examining its properties. The use of amatol ultimately became universal for Land Service shell, bombs, and other munitions, on account of its efficiency, its cheapness (one-third of cost of picric acid), and the small consumption of nitric acid in its manufacture as compared with picric acid. The merits of amatol commended it to other countries, so that it was adopted by the United States as their high explosive, and was being taken up by France and Italy near the end of the War.

In this country, the enormous output of 4,000 tons of amatol a week was reached, for which

ammonium nitrate had to be produced in corresponding quantity. This was obtained by suitably modifying the ammonia-soda process, and also through calcium nitrate, formed from sodium nitrate and calcium chloride, but as the demand increased special factories were erected for making ammonium nitrate by the direct process of double decomposition of sodium nitrate and ammonium sulphate, according to the process worked out by Freeth on the basis of the phase-law relationship of these salts in solution at the appropriate temperatures.

Although picric acid receded in importance during the War, notable work was done in starting and operating factories for the synthetic production of phenol from benzene, as the quantity of phenol from the distillation of coal tar was insufficient. Another method of avoiding phenol, due to Green, was further to nitrate dinitrophenol made by hydrolysing dinitrochlorobenzene. Considerable improvements were made in the methods of the nitration of phenol, which previously had been wasteful.

The only other explosives for military purposes produced in quantity during the War were ammonium perchlorate, for which two factories were erected to produce that substance by electrolysis, and mercury fulminate, required in enormous quantities as an initial detonant for all kinds of fuses and caps.

Most of the war factories have been dismantled, but fortunately a record of their operation and technical advances has been saved. In the two volumes on "Costs and Efficiencies," Quinan gives tabularly and by diagrams the results of operating them that were periodically put before the managers of the explosives factories in his charge, with the object of displaying features which were capable of improvement. The plan was eminently successful in reducing costs of production and usage of material.

A series of memoirs published by the Stationery Office has been prepared by Macnab dealing with the technical records of explosives supply. These studies include such subjects as the manufacture of trinitrotoluene, manufacture and treatment of acids, synthetic phenol and picric acid, solvent recovery and heat transmission, and form a valuable addition to the literature of technical chemistry, useful, not merely to the specialist in explosives, but also to the teacher and to the general chemical technologist.

In the field of practice the advantage of the organised application of chemical technology was demonstrated on the largest scale, and with results which were far reaching for their immediate object, and which, it is to be hoped, will be reflected in improved technical method in British chemical industry.

The production of blasting explosives had to be kept at the normal level during the War to maintain the output of the mines, the proportion of nitroglycerine being diminished. The most important advance was the manufacture of blasting gelatine and gelatinised nitroglycerine explosives generally without heating the mixture of nitroglycerine and nitro-cellulose, by the aid of a small quantity of a substance to promote gelatinisation (Rintoul and Cross). The new process of cold gelatinisation, besides being cheaper, is safer and permits of an increased output. Some of the gelatinisers also have stabilising properties, and are proposed for use in the manufacture of propellants (Nathan, Rintoul, and Baker).

Another investigation at Nobel's Ardeer factory has shown that low heat tests of nitroglycerine are due to the presence in the nitroglycerine of chlorine derivatives of tetranitromethane. On washing the nitroglycerine with a solution of sulphite of soda these impurities are destroyed, when the product passes the heat test without difficulty.

As showing the extent of the replacement of gunpowder by high explosives in mining, the

quantities for 1913 and 1922 respectively were 17,000,000 and 11,600,000 lb. for gunpowder, and 16,600,000 and 21,600,000 lb. for other explosives.

Research.—The viscosity of cellulose and of nitrocellulose, as has been indicated in connection with the manufacture of R.D.B. cordite, was investigated. The apparatus chosen by Gibson, Masson, and their assistants was the falling sphere viscosimeter, for which a technique was worked out, a solution of cuprammonium being used as solvent for cellulose, ether–alcohol for soluble nitrocellulose, and acetone–water for guncotton. The results expressed in C.G.S. units disclosed a point of lowest viscosity which is the best ratio for solution of the nitrocelluloses by ether–alcohol and by acetone–water; the effect of the nitrogen content was examined, and the subject was considered in the light of the expressions that have been advanced connecting concentration of the disperse phase with viscosity.

Trinitrotoluene also received much attention at the Research Department, Woolwich, from the points of view of organic and physical chemistry and of its explosive properties. Thus Brady made an exhaustive study of the products of nitration of toluene, especially the unsymmetrical isomerides which arise from the further nitration of metanitrotoluene. The possibility of utilising the unsymmetrical trinitrotoluenes occurring as impurities in crude trinitrotoluene and of converting them into useful products was considered.

The properties of the isomerides of trinitrotoluene were investigated in various aspects. Gibson determined the setting-point curves of mixtures of the isomerides, and was able to deduce from the setting-point of the crude product of nitration the proportion of material liquid at different temperatures of storage. A study of the heat of formation of the mono-, di-, and tri-nitrotoluenes by Garner brought out interesting relationships between this constant and the stability towards heat and the sensitiveness to impact. The heat and gases evolved when trinitrotoluene and other explosives are truly detonated in a calorimetric bomb specially adapted to withstand the high pressures developed has been determined by Robertson and Garner.

By the method of Rotter, in which is measured the gas evolved from an explosive subjected to impact while enclosed in a chamber with a manometer attached, the sensitiveness of explosives to a blow has been measured, and the personal element in assessing results greatly eliminated. An important development in determining the pressure developed by explosives was the application of the principle of Hopkinson's pressure bar by Quinney at Woolwich. By its aid not only was information on the phenomena of detonation gained, but it was possible to arrange explosives in order of their violence, and to test in a rapid manner the efficacy of mechanisms containing explosives. It is now being used also in the investigation of blasting explosives.

In connection with amatol, Lowry, Perman, and Early investigated the change of state of ammonium nitrate on heating, of which peculiarity advantage was taken in making the explosive; they also determined the effect on the freezing point of the presence of other salts likely to occur from the manufacture, a feature also with a practical bearing.

The theory of explosion of propellants from the thermodynamical point of view has been treated by Henderson and Hassé, who, without making any arbitrary assumption as to the relation between pressure and volume behind the projectile, have calculated the indicator diagram of the gun from the constants of the propellant and of its products. Hadcock and Mansell have also made contributions on the ballistics of propellants.

In a recent lecture to the Chemical Society by the author will be found collected many of

the constants of explosive substances, regarded especially in respect to the constitution of the bodies. The scope of this review will be indicated by the following headings : heat of formation, heat of detonation, gases evolved, stability to heat, temperature coefficient of decomposition, sensitiveness to impact, rate of detonation, and pressure developed. The amatols are also considered under these various aspects, it being shown, *inter alia*, that the ammonium nitrate does not act simply as a supplier of oxygen to the trinitrotoluene which is deficient in this respect, but that it is in itself an explosive.

In general, it may be said that the above researches, inaugurated as most of them were in connection with definite and often pressing problems, and frequently carried only a little beyond the stage of their immediate usefulness, have afforded information on fundamental questions and given a clearer knowledge of the chemistry and physics of explosives.

THE CHEMISTRY OF PHOTOGRAPHY

By Walter Clark, M.Sc.

Foreword by Sir Wm. J. Pope, K.B.E., F.R.S.

Few scientific problems have resisted elucidation by experimental workers so successfully as have those which lie at the foundation of the art and practice of photography. An enormous expenditure of ingenuity and perseverance has been incurred in attempts to ascertain the principles and mechanisms which underlie and determine the action of light upon the silver salts used in photography, but although a slow and certain progress is to be recorded, little fundamental to the explanation of the photographic process has yet been achieved.

Whilst this uncertainty prevails regarding the nature of photographic action, it must not be supposed that no progress is being made in photography as a branch of applied science; in fact, rapid developments are even now taking place, and the photography of to-day is a very different subject from that of even ten or twenty years ago. Much progress has been made in two distinct branches of the subject, which may be distinguished, first, as that of the mechanical section and, secondly, as that which includes the physical or chemical side of photography as a technological subject.

The last few years have seen rapid developments in the manufacture of photographic lenses, particularly in this country. Obviously, since photographic action consists in the action of light, the photographic effect produced on a plate exposed in the camera is proportional in quantity to the amount of light which reaches the plate, and this quantity is determined by the effective aperture of the lens fitted to the camera. Not many years ago the best photographic lenses ordinarily available had an effective aperture of one-eighth of the focal length; to-day, lenses of British manufacture with an effective aperture of more than one-third of the focal length can be obtained. That is to say, lenses produced to-day yield a sharply-defined image on the photographic plate with an exposure only about one-tenth as long as that necessary with the best procurable lenses of ten or twenty years ago. This appears as a great achievement, especially when viewed in the light of the scientific acumen essential to the evolution of a satisfactory specification for the materials and curvature of the lens and of the mechanical dexterity required in the actual manufacture of the lens itself in accordance with the specification.

Although much might be added concerning recent progress on the mechanical side of photography—on high-speed cinematography, photomicrography, *X*-ray photography, etc.—the need for brevity makes it necessary to pass rapidly to illustrations of photographic progress of a physical or chemical nature.

The rapid dry plate first introduced by the late Sir Joseph Swan, which ultimately becomes the photographic negative, is only sensitive to light from the blue or violet region of the spectrum. The camera provided with an ordinary dry plate thus sees and records a scene in much the same way as we should visualise it through deep blue spectacles. The plate being sensitive only to blue light, which to us is not highly illuminating, the blues appear bright in an ordinary photograph, whilst the yellows and reds, which to us appear brilliant, are reproduced as black or at least dark in the photograph. The ordinary photographic rendering in monochrome of a multi-coloured scene is thus an inversion of that effected by the human eye; in the photograph, the bright reds and yellows appear black, and the dull, pure blues, dark to us, are shown as light in tone. The inversion of colour rendering in monochrome which occurs as between the photograph and the human eye is responsible for the fact that a photograph is

immediately recognised as such when exhibited; our life-long habitude of inspecting photographs which represent the green grass, the yellow narcissus, and the red rose as black, has dulled our senses but has at least enabled us to distinguish instinctively between a photographic reproduction of a scene and its appreciation by the eye or its representation by the black and white artist.

It is clear that if photography is to serve a function as a means (1) of reproducing a coloured scene in monochrome with a correct mode of translating into monochrome the grades of luminosity of a multi-coloured object and (2) of furnishing a means of reproducing a coloured scene in natural colours, one development is essential. Means have to be found for making the photographic plate sensitive to light of all colours; this having been done, it is possible (1) to obtain a correct rendering in monochrome of a multi-coloured object and (2) to devise mechanical methods for obtaining a correct photographic reproduction in the natural colours of a multi-coloured scene. The necessity for this development was first realised by the late Clerk-Maxwell, the Cavendish Professor in the University of Cambridge, in 1861, and his experimental attempts to put his new views into practice were shown at the Royal Institution in that year.

Photographic plates can be made to-day which are sensitive to light of all colours, and by appropriate mechanical devices these can be used for the preparation (1) of correct renderings in monochrome of parti-coloured scenes and (2) of very accurate representations in the natural colours themselves of coloured objects. It is quite certain that in a few years' time no one will tolerate the ordinary photographic portrait, with its false rendering in monochrome of colour values, and that the modern photographer will provide his clients with portraits which, if not necessarily artistic productions, will at least constitute a correct translation into monochrome of the colours presented by the sitter.

This subject is an entrancing one, and has had many developments. Thus, it is known that the atmosphere is less transparent to blue light than to light of longer wave-length, such as the deep red. Consequently, the blue-sensitive photographic plate gives a picture of a distant scene in which the far details are more confused by haze than they are by visual inspection, the eye utilising, in the main, yellow light which is of longer wave-length than the blue. But a photographic plate, rendered sensitive to the deep red of very long wave-length, could be used to produce a photograph of a distant scene in which, owing to the greater transparency of the atmosphere for red than for yellow light, the distant detail is revealed with far more distinctness than to the human eye. This principle found a valuable application during the recent War; our aeroplane observers used photographic plates highly sensitive to red light, made their exposures through red screens which cut off all light of shorter wave-length, and obtained photographic records in which distant detail was depicted with a distinctness and freedom from blur which were quite impossible even by visual observation.

W. J. P.

Of the many subjects which have a wide practical application to science and industry in general, there is probably none which is so little understood as that of photography. In fact, although photographic processes of some kind or other have been employed for nearly a hundred years, it is only within the past twenty years or so that it has been possible to make attempts to ascertain the nature of the photographic process, and to place the making of

practically useful photographic materials on a strictly scientific basis. The modern dry plate or film is a very efficient article, but its excellence is due rather to the application of laboriously acquired empirical knowledge than to that of scientific principles. During the present century, however, the scientific aspect has been investigated by competent research workers in England, America, and on the Continent, and enormous strides have been made. The formation of the British Photographic Research Association in 1918 gave a fresh impetus to investigations in this country. But the solution of the basic problems is as yet far from being in view.

The modern photographic material must be considered as having its ultimate origin in the experiments of Wedgwood and Davy in 1802, concerning the action of light on paper treated with a solution of silver nitrate. Its progress from these simple observations to the Daguerreotype process, the use of glass and celluloid instead of paper as a support for the light-sensitive material, the wet and dry collodion processes, and ultimately the use of gelatin as the medium for the sensitive substance, forms a very fascinating story. The greatest impetus was given to the perfecting of the modern photographic material by the introduction of gelatin as the medium by Maddox in 1871, and by the discovery of the advantages of " ripening " the emulsion made by Bennet in 1878. It was about this period that the modern plate and film had their immediate origin, and that the modern speculations regarding the fundamental processes of photography began to take form.

The whole process of photography is based on the apparently simple fact that certain salts of silver undergo some change when they are exposed to light, and, under ordinary conditions, only to light of short wave-length, blue, violet and ultra-violet. Nearly all salts of silver are acted upon by light, but in the majority of photographic processes the halogen salts have been found to be the most suitable, and are almost exclusively employed.

The light-sensitive photographic material, whether plate or film or paper, consists of a support on which is coated the sensitive " emulsion." The term " emulsion " was used when the disperse character of the sensitive system was not realised, and it is now known to be a misnomer. The " emulsion " is in reality a " suspension " of fine crystalline particles of silver halide in a medium of gelatin, or, in certain cases, of collodion. Many colloidal substances, such as gelatin, albumin, collodion, agar-agar, and silicic acid, have been investigated as media for holding the sensitive silver halide, but of these gelatin and collodion alone have proved of practical value, and only by the use of gelatin is it possible to obtain satisfactory materials having a high degree of sensitivity to light in conjunction with other necessary properties.

The various types of photographic material, the utility of which depends upon the action of light on silver salts, may be divided into two broad classes. The first class consists of those materials in which the action of light is to bring about a visible change in the sensitive material as a result of photochemical decomposition of the silver salt, giving a visible yield of metallic silver which forms the photographic image. To this class of material belong the well-known " printing-out " papers, the sensitive material being usually a mixture of the chloride and citrate of silver.

The second class is composed of those materials in which the primary action of light is to give an invisible product known as the " latent image," which requires the application of a reducing agent—the " developer "—to render visible the effect of the light action. This class includes ordinary plates and films, in which the sensitive material is silver bromide, or more usually the bromide together with a small proportion of silver iodide, and so-called " development papers " and lantern plates, in which use is made of the bromide and chloride of silver.

The investigations of the Continental schools of photographic research have been directed mainly to the solution of problems concerning " printing-out " materials, whereas the chief British investigators have confined their attention to the more important problems connected with the " latent image " and the properties of the members of the second class mentioned above.

A survey of the development of ideas concerning the photographic process shows two distinct periods, with a sort of transition period between them. The first period extends up to the latter years of the last century, culminating in the classical work of Hurter and Driffield in England, and the second period includes theories which have been developed in the past few years, and which are now being actively worked out. The former theories assumed a homogeneity and continuity of the light-sensitive emulsion, of the incident radiation, and of the developed image, whereas the newer theories recognise the disperse character of emulsions and the possibility of heterogeneity of the light and of the grains in the emulsion.

The rapid strides which have been made in the direction of solving the riddle of photographic sensitivity have been due largely to the use of the microscope as an instrument of investigation. By its aid it was shown years ago that the sensitive emulsion consisted of individual particles of silver halide having in most cases definite external crystalline forms. *X*-Ray analysis has shown that the chloride and bromide of silver crystallise in the cubic system, whereas with silver iodide both hexagonal and cubic forms exist. The size of the emulsion grains varies from being so small as to be irresolvable by the highest-power microscope, up to about 10μ across in the case of the biggest grains, although the emulsions used in practice do not often contain crystals larger than about 3μ. The *X*-ray method of analysis has shown that the smallest visible grains, which appear like small spheres in the microscope, although not exhibiting an external crystalline shape, possess the same lattice structure as the larger grains of definite shape. In an ordinary emulsion, the number of grains in 1 sq. cm. of normally coated plate is of the order of 10^9.

After the discovery of the essentially disperse character of the emulsion, it came to be recognised that the individual silver halide grain is the fundamental unit of a photographic emulsion. This is indicated beyond doubt by the work of Slade and Higson, Toy, Svedberg, and the research workers of the Eastman Kodak Co. Every grain in the emulsion has its own individual sensitivity, and is capable of being affected by light and developed quite independently of any other grains in its neighbourhood. It would appear, from certain results which have been obtained, that in the case of " clumps " of grains, if one grain of the clump is so changed by the action of light that it is capable of being reduced by a developer, then the whole clump is made developable. If this were the case, then the clump would act as a single grain and would have to be considered as one individual unit. Such cases, however, are not general and in many emulsions grains can be found apparently in contact, one of which is developable without its reducibility being transferred to the contiguous grain.

If a photographic plate is exposed progressively to light of increasing intensity, then on development a black silver deposit will be obtained, with the amount of silver per unit area increasing in the direction of increasing exposure. The silver deposits absorb varying amounts of light, according to the amount of silver present, and by measuring the light absorption of these areas, a numerical specification of the blackening corresponding with different exposures to light is obtained. The degree of blackening is denoted by the " density " which is defined as the logarithm of the reciprocal of the fraction of light transmitted. If the density of each

step is plotted against the logarithm of the corresponding exposure, an S-shaped curve is obtained which is known as the " characteristic curve " of the plate. This curve is of great practical importance as indicating the " speeds " and contrast-rendering properties of the plate.

Examination of the characteristic curve shows that with increase in the exposure of a plate to light an increasing amount of silver is formed on development. Now, this silver results from the reduction of light-affected grains, and its increase with increasing exposure could be due either to an increase in the number of grains made developable, or else to an increase in the partial development of every grain. The former has been shown to be actually the case. That is, with increasing exposure to light an increasing percentage of grains is made developable.

It is clear, then, that different grains in one given emulsion require different exposures to light to render them capable of reduction by a developer. This immediately leads to the question, " Wherein does the different sensitivity of different grains in one emulsion lie? " This is the problem that workers during the past few years have been endeavouring to solve.

Now, it is usually found that with an emulsion containing a very small range of grain-sizes the range of their sensitivities to light is narrow, whereas with a large variation in grain size a big sensitivity range is obtained. Examination of ordinary commercial plates shows that, in general, with the plates of highest sensitivity the average grain size and the distribution of sizes is bigger than is the case with plates of lower speed. It is now known that there is not necessarily a strict parallelism between these two factors, since cases have been found in which the converse holds. The observations, however, led to the suspicion that there was some relationship between the size of a grain and its sensitivity—the bigger the grain, the higher was its sensitivity to light. That this was not necessarily the case was proved by experiments of Toy with flat, triangular grains all of identical shape and size from one emulsion, and all orientated equally to the incident light. By counting the percentages of grains changed instead of measuring densities, it was shown that the usual S-shaped characteristic curve was obtained, thus indicating that variation in geometrical properties of the grains is not an essential feature of an emulsion in order that it may give the usual type of curve.

Since, therefore, grain sensitivity is not necessarily a function of grain size, we must explain the different sensitivities of apparently identical grains in one emulsion as due either to a variation in the composition of the individual grains, or else to some peculiarity of the light action and its mode of absorption.

The situation thus created led in 1922 to an important advance when it was shown by Svedberg in Sweden and Toy in England that even more fundamental than the emulsion grains themselves are the so-called " reduction centres " of the grains. If the development of exposed grains is stopped suddenly in its early stages, it is found that the grains have started to develop at a few points only, and not generally over their surfaces. The points at which development is initiated are known as the " reduction centres " of the grains. Observations on the localisation and distribution of the centres have been made, and it has been established that : (1) The centres are distributed among the grains entirely haphazard, following the laws of chance. (2) The centres are distributed, on the average, uniformly over the surface of spherical grains, but in the case of flat grains they are concentrated on the edges.

The question then arose, and it is one of vital importance for photographic theory, as to the origin of the reduction centres. It is clear that they could have their ultimate origin either in the making of the emulsion, in the exposure to light, or in the development process.

It has been shown that this last possibility cannot hold, since for one given time of development the number of centres is a function of the exposure to light. The other two possibilities have given rise to the biggest controversy in the history of photographic theory, and although the problem is by no means definitely settled, there is overwhelming evidence in favour of the ultimate origin of the centres residing in the process of manufacture of the emulsion.

It was assumed, on the one hand, that the formation of the reduction centres was a result of a discrete structure of light, and theories which fit some of the facts have been developed, based on Einstein's modification of Planck's light quantum theory. Foremost among these is Silberstein's idea of "light-darts," which assumes that the necessary condition for the formation of a reduction centre is the impact of one or more "light-darts" on the silver halide grain.

The other definite point of view, the chief exponent of which is Toy, is that as a result of the method of manufacture of the emulsion there is present at points in the grains some material which is not the ordinary silver halide, and that the function of the light is to change the grains at these points in some way so as to render them susceptible to the reducing action of the developer. Whether this "foreign" material itself is more sensitive to light than the silver halide, or whether it merely acts as a sort of photocatalyst in increasing the sensitivity of the silver halide, is not yet clear, although it is extremely probable that the latter represents the actual facts.

A considerable amount of evidence has now been accumulated which indicates that the "light-dart" idea is absolutely untenable and that Toy's suggestions are nearer the truth. For example, a large number of chemical reagents, among which may be mentioned sodium arsenite (NaH_2AsO_3), hydrogen peroxide in neutral solution, ozone, an acid solution of stannous chloride, and sodium hypophosphite, have been found to duplicate the action of light on a silver bromide–gelatin plate. Now, since none of these reagents reacts with ordinary silver bromide, it must be concluded that there is present at the surface of the silver bromide grains some other substance with which they can react to give the nucleus necessary for development of the silver bromide.

Further, it has been found possible to reduce the sensitivity of plates to a low minimum, which is approximately the same for all types of silver bromide emulsion, by bathing the plates in a solution of chromic acid, thus indicating that there is a limited amount of "foreign" substance in the grains, to which their high sensitivity is due.

We have dealt rather fully with the question of sensitivity, because it is the basis of the whole process of photography. The advances which have been described have all been made during the past five years, and the investigations are still being actively pursued. Little or nothing is known as to the nature of the material to which the high sensitivity of an emulsion is due. The manufacture of an emulsion is an intricate process, necessitating the use of such a complicated chemical substance as gelatin, and any slight variation in the method of manufacture is capable of bringing about enormous alterations in the properties of the finished material. Variation in the gelatin employed brings about large fluctuations in sensitivity to light, and even if the physical properties of emulsions, such as grain-size distribution, weight of silver per unit area of coated plate, and so on, are controlled so as to remain constant, slight alterations in the chemical constituents are able to effect marked changes in speed. Is the sensitivity due to the inorganic materials in the gelatin, to the organic degradation products present in the gelatin, or to something else not connected with the gelatin which merely acts

as a protective colloid? These are the problems which it is of the utmost importance to solve. In the case of "print-out" emulsions, it is probable that the gelatin acts as a sensitiser by combining with the halogen liberated by the photo-chemical decomposition of the silver salt, thus upsetting the equilibrium which would otherwise be set up between silver and halogen, but it is extremely doubtful whether such an effect is of much importance in connection with the latent image. The quantities of energy necessary for its formation are excessively minute.

Though the most important problem of photographic theory is that of sensitivity, there are many others of great practical importance. Foremost among these is that of the development process. A photographic developer is a solution of a reducing agent which will reduce to metallic silver the grains of an emulsion which have been changed by the action of light, but which will not reduce the unaffected grains. The developer will only reduce the silver halide in the presence of a nucleus, which is probably formed by the light during exposure. When once one such nucleus has been formed in a grain, the whole grain becomes completely reducible. The earlier views, that development was merely the result of chemical reaction between the silver bromide in solution and the developer, are now giving place to ideas in which adsorption factors play the predominant part. The tendency, now, is to regard the first stages of development as consisting in selective adsorption of the developer to the exposed silver halide grains, resulting, according to Bancroft, in selective peptisation of the solid phase, or else in intramolecular rearrangement of the adsorption complex, giving rise directly or indirectly to the "nucleus" necessary for the reaction $Ag^{+} + \ominus = Ag_{metal}$ to occur.

It is extremely probable that adsorption plays a far larger part in photographic processes than has been hitherto realised. Sensitivity and development are undoubtedly bound up to a large extent with adsorption processes, and it is also in the field of colour-sensitisation that adsorption is employed to bring about certain desired effects. It has been pointed out before that the ordinary plate is only notably sensitive to light rays of short wave-length. That the sensitivity is not confined merely to the blue end of the spectrum, however, is indicated by the fact that it is not possible to find any threshold wave-length above which no photographic action occurs, provided a sufficiently prolonged exposure is given. For all practical purposes, however, ordinary plates may be regarded as insensitive to the red end of the spectrum. It is this very low sensitivity to rays of long wave-lengths which allows of the use of red lamps in the dark room.

However, by bathing the plates in solutions of certain dyes, such as eosin, fluorescein, erythrosin, etc., or else by incorporating the dyes in the emulsion before coating the plates, it was found possible to extend the sensitiveness of plates to yellow and green light. As a result of investigations in recent years, in particular by Pope and Mills at Cambridge University, numbers of dyes have been prepared which enable the sensitiveness of plates to be extended well into the red end of the spectrum, thus making panchromatic photography possible. The action of sensitising dyes is still in doubt. The added spectral sensitivity of the silver halide is approximately parallel with the absorption spectrum of the dye, but the maximum is displaced somewhat towards the long wave-lengths. There is a limit to the sensitiveness of plates to short wave-lengths which is imposed by the absorption of the ultra-violet rays by the gelatin of the emulsion. By dissolving away most of the gelatin in the plate by means of dilute acid, this absorption has been partly eliminated, and the usefulness of plates extended well into the ultra-violet. By various modifications it is now possible to obtain plates sensitive to light of wave-lengths between 1850 Å.U. and over 7000 Å.U.

The employment of colour-sensitive plates imposes a greater restriction on the amount and quality of the light used to illuminate the dark room. For panchromatic materials special green safe-lights may be used, but the illumination permissible is very low, and it is preferable to work in absolute darkness. Lüppo-Cramer, however, has recently discovered that certain dyes, notably phenosafranin, at a very low concentration, are capable of exerting a desensitising action without affecting the latent image. This enables plates to be developed in yellow light after treatment with the dye solution. The mechanism of the action of these desensitisers is little understood, but their employment shows promise of great value, particularly in the sphere of *X*-ray photography.

It is not possible in a short article to deal with the many other unsolved problems connected with the photographic process. In the fields of colloid chemistry of photographic materials, the physical chemistry of development, fixation, intensification and reduction, sensitometry and tone reproduction, much more work remains to be done and is now being steadily carried on. Though it may appear from the above summary that nothing definite is yet known about the fundamental principles of photography, yet the advances which have been made in unravelling the tangle have been enormous, although confined mainly to the past few years. In solving the riddles of photography, British investigators have played by far the biggest part, and it is to such men as Hurter and Driffield, Sheppard and Mees,* and the research workers of the British Photographic Research Association in this country and the Eastman Kodak Co. in America that most of our present knowledge is due.

The cinema industry now absorbs by far the majority of photographic materials, but the use of photography in astronomy, physics and chemistry, and metallurgy, surveying on land and from the air, in printing processes, in surgery, and even in the detection of crime, places it in the foremost rank among the practical sciences.

* Although Drs. Mees and Sheppard are now members of the Eastman Kodak Co., it must be remembered that they are Englishmen trained at University College, London.